UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Mechanical Engineering

THE DEVELOPMENT OF CARBON NANOTUBE/CARBON NANOFIBRE FROM POLYACRYLONITRILE ELECTROSPUN NANOFIBRE PRECURSOR FOR ELECTRONIC APPLICATIONS

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A thesis submitted
in fulfilment of the requirements for the degree of Master of Science
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DECLARATION

I declare that this thesis entitled "The Development of Carbon Nanotube/Carbon Nanofibre from Polyacrylonitrile Electrospun Nanofibre Precursor for Electronic Applications" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :…………………………………………………...

Name :…………………………………………………...

Date :…………………………………………………...

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Mechanical Engineering

Signature	:	....
Supervisor Name	:	....
Date	:	....

DEDICATION

To my beloved mother and father

ABSTRACT

Carbon nanofibre (CNF) have attracted much attention among researchers due to their excellent properties such as high mechanical strength, thermal and electrical conductivity. CNF have been proposed for various applications such as filtration, smart material, tissue engineering, fuel cell, capacitors and sensors. Recently, electrospinning technique followed by pyrolysis process of the precursor material has been proposed as a simple and economic alternative for fabricating CNF. In this study, the best parameters on fabrication process of CNF with and without the inclusion of multi-walled carbon nanotubes (MWCNT) fillers were determined and their properties were characterised. MWCNT was selected due to its superior electrical properties. Previously, considerable amount of effort have been made on studying the physical, chemical, and mechanical properties of electrospun CNF. However, there are limited studies dedicated to investigating the electrical properties of the CNF especially in terms of conductivity, complex permittivity (dielectric constant and loss factor) and loss tangent. Therefore, the scope of this research is to investigate the relationship of electrical properties with physical and chemical properties of the fibres. Polyacrylonitrile (PAN) precursor nanofibre were prepared using electrospinning technique. The best parameters for electrospinning were investigated by preparing the samples at electrospinning distances of 5 cm to 30 cm and applied voltage of 5 kV to 20 kV. Furthermore, the best pyrolysis process was determined by varying the carbonisation temperature of 800 ºC, 1000 ºC and 1200 ºC with heating rate of 3 ºC/min and 5 ºC/min in a nitrogen filled furnace. As the optimum parameters were achieved, nanofibre samples with and without MWCNT were prepared. The characterization of the electrospun CNF was carried out using scanning electron microscopy (SEM), transmission electron microscope (TEM), ImageJ software, Fourier transform infrared spectroscopy (FTIR), four-point probe methods and dielectric probe. Based on fibre diameter, morphology, and deposition amount; the optimum electrospinning distance was found to be between 10 cm to 20 cm with an applied voltage between 15 kV to 20 kV. The results also suggest that increase in carbonisation and heating rate during pyrolysis process would increase the rate of elimination of non-carbon elements. This is evidenced by flatter FTIR spectrum and higher electrical conductivity of the samples which were carbonised at 1200 ºC and heating rate of 5 ºC/min. The electrical conductivity of CNF was significantly increased with the inclusion of MWCNT. The highest electrical conductivity was showed by CNF with 0.1 wt% of CNT with value 155.90 S/cm. However, samples with higher amount of MWCNT (> 0.1 wt%) showed reduced electrical conductivity to 21.56 S/cm. This could be explained by the formation of broken fibre network and agglomeration of MWCNT as observed using SEM and TEM. Finally, complex permittivity values of pure CNF and MWCNT-filled CNF were highest with dielectric constant value of 338.38 and loss factor value 488.72 at 1 GHz frequency. The knowledge gained from this study would extend the use of electrospun nanofibre in electronic applications such as sensors and other nano-sensing applications.

ABSTRAK

Karbon nanoserat (CNF) telah menarik perhatian ramai penyelidik kerana sifat-sifatnya yang bagus seperti kekuatan mekanikal, kekonduksian termal dan elektrik yang tinggi. CNF telah dicadangkan untuk berbagai aplikasi seperti penapisan, bahan pintar, kejuruteraan tisu, sel bahan, kapasitor dan sensor. Pada masa ini, teknik pemintalan elektro diikuti dengan proses pirolisis untuk prekursor serat yang disintesis telah dicadangkan sebagai satu alternatif yang mudah dan ekonomi untuk menghasilkan CNF. Dalam kajian ini, parameter terbaik untuk proses fabrikasi CNF dengan dan tanpa penambahan nanotiub karbon berbagai dinding (MWCNT) ditentukan dan sifatnya dicirikan. Sebelum ini, pelbagai usaha telah dilakukan untuk mengkaji sifat fizikal, kimia dan mekanikal bagi CNF terpintal. Walau bagaimanapun, terdapat kajian yang terhad khusus untuk menyiasat sifat elektrik CNF terutamanya dalam soal kekonduksian, ketelapan kompleks (pemalar dielektrik dan faktor kehilangan) dan tangen kehilangan. Oleh itu, skop penyelidikan ini adalah untuk mengkaji hubungan sifat elektrik dengan sifat fizikal dan kimia. Prekursor nanoserat Poliakronitil (PAN) telah dihasilkan menggunakan teknik pemintalan elektro. Parameter terbaik untuk proses pemintalan elektro disiasat dengan menyediakan sampel pada jarak elektrospinning 5 cm hingga 30 cm dan voltan terpakai 5 kV hingga 20 kV. Tambahan pula, proses pirolisis terbaik ditentukan dengan mengubah suhu karbonisasi 800 ºC, 1000 ºC dan 1200 ºC dengan kadar pemanasan 3 ºC / min dan 5 ºC / min dalam relau yang diisi dengan gas nitrogen. Oleh kerana parameter optimum telah dicapai, sampel nanoserat dengan dan tanpa CNT telah disediakan. Pencirian CNF terpintal dilakukan menggunakan mikroskop pengimbasan elektron (SEM), mikroskop penghantaran elektron (TEM), perisian ImageJ, Fourier transform spektroskopi inframerah (FTIR), kaedah empat titik prob dan prob dielektrik. Berdasarkan diameter serat, morfologi dan jumlah pemendapan, jarak optimum pemintalan elektro adalah antara 10 cm hingga 20 cm dengan voltan yang dikenakan antara 15 kV hingga 20 kV. Hasilnya menunjukkan peningkatan kadar karbonisasi dan pemanasan semasa pirolisis akan meningkatkan kadar penghapusan unsur-unsur bukan karbon. Ini dibuktikan dengan spektrum FTIR yang lebih rata dan kekonduksian elektrik yang lebih tinggi daripada sampel yang berkarbonat pada 1200 ºC dengan kadar pemanasan 5 ºC/min. Kekonduksian elektrik CNF meningkat dengan ketara setelah CNT dimasukkan. Kekonduksian elektrik tertinggi telah dihasilkan oleh CNF dengan 0.1 wt% CNT dengan jumlah 155.90 S/cm. Bagaimanapun, sampel dengan jumlah yang lebih tinggi mengandungi CNT (> 0.1 wt%) menunjukkan kekonduksian elektrik yang rendah kepada 21.56 S/cm. Ini dapat dijelaskan oleh pembentukan rangkaian serat pecah dan pengumpulan CNT seperti yang diperhatikan menggunakan SEM dan TEM. Akhirnya, nilai kebolehtelapan kompleks CNF dan CNF yang dipenuhi CNT adalah tinggi dengan jumlah pemalar dielektrik 488.72 dan jumlah faktor kehilangan 488.72 pada frekuensi 1 GHz. Pengetahuan yang diperoleh dari kajian ini akan memperluaskan penggunaan nanoserat terpintal dalam aplikasi elektronik seperti alat pengesan dan aplikasi nanopengesan yang lain.

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LIST OF ABBREVIATIONS

ACNF	-	Activated Carbon Nanofibre
CNF	-	Carbon Nanofibre
CNT	-	Carbon Nanotube
CNT	-	Chemical Vapour Deposition
DMF	-	Dimethylformamide
DWCNT	-	Double-wall Carbon Nanotube
FE-SEM	-	Filed Emission Electron Microscpe
FTIR	-	Fourier Transform Infrared Spectroscopy
MWCNT	-	Multi-wall Carbon Nanotube
PAN	-	Polyacrylonitrile
PANI	-	Polyaniline
PLA	-	Polyactic Acid
PU	-	Polyurethanes
PVA	-	Polyvinyl Alcohol
PVDF	-	Polyvinylidene Flouride
SEM	-	Scanning Electron Microscope
SWCNT	-	Single-wall Carbon Nanotube
TEM	-	Transmission Electron Microscopy
VNA	-	Vector Network Analyzer

LIST OF PUBLICATIONS

The research papers produced and published during the course of this research are as follows:

Journals:

1. N. A. Munajat, A. H. Nurfaizey, M. H. M. Husin, S. H. S. M. Fadzullah, G, 2018. The effects of different carbonization temperatures on the properties of electrospun carbon nanofibre from polyacrylonitrile (PAN) precursor. *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences (ARFMTS)*, 2(49), pp. 85-91. *(Scopus).* (published)
2. N. A. Munajat, A. H. Nurfaizey, A. A. M. Bahar, K. Y. You, S. H. S. M. Fadzullah, G. Omar, 2018. High frequency dielectric analysis of carbon nanofibre from PAN precursor at different pyrolysis temperatures. *Microwave and Optical Technology Letters (MOTL)*, 60(9), pp. 2198-2204. *(Scopus/ISI).* (published)

Conference papers

1. N.A. Munajat, A.H. Nurfaizey, S. H. S. M. Fadzullah, 2018. The preparation and morphological investigation of polyacrylonitrile electrospun nanofibre with different loading of carbon nanotube. *1st Colloquium Paper: Advanced Materials and Mechanical Engineering Research (CAMMER'18)*. (published)
2. N. A. Munajat, A. H. Nurfaizey, S. H. S. M. Fadzullah, G. Omar, J. Jaafar, N. S. A. Roslan, 2017. Fabrication and characterization of carbon nanofibre from

polyacrylonitrile precursor. *Proceedings of Mechanical Engineering Research Day 2017*, Melaka, Malaysia, pp. 362-363. (published)

CHAPTER 1

INTRODUCTION

1.1 Research background

Recently, there was a growing research interest in nanofibrous materials as evidenced by the increasing number of publications with regard to nanofibre. One of the main reasons for this growing trend is due to the unique properties and superior capabilities of nanofibre. Nanofibrous materials have been proposed for various applications such as filtration, sensor, drug delivery, super capacitors and energy storage (Ramesh Kumar et al., 2012, Lee et al., 2014, Su et al., 2014, Zhou et al., 2014, Myung et al., 2015). Nanofibre is defined as ultrafine fibre with average fibre diameters typically in the range from 100 nm to a few microns.(Nataraj et al., 2012). At this scale, nanofibre offer unique properties such as high surface area, high porosity, light weight, as well as outstanding structural and mechanical properties (Zhang et al., 2014, Haider et al., 2015, Poveda and Gupta, 2016, Yalcinkaya et al., 2016).

One of the nanofibre research areas that has been particularly interesting is in the synthesis of carbon nanofibre (CNF). CNF is similar with other one-dimensional nanostructures such as nanotubes and nanowires in terms of high length-to-diameter ratio (Pashaloo et al., 2009). Traditionally, carbon fibre materials can be prepared by using several processes including post heat treatment of precursor materials. Precursor materials can be natural or synthetic materials which fulfil certain condition such as the ability to withstand high temperature during pyrolysis process in an inert environment (Cho et al., 2007). Polyacrylonitrile (PAN) precursor is one of the most popular precursor materials for the fabrication of CNF. In term of processing method, electrospinning has been opted as the preferred choice for fabricating nanofibre (Huang, 2009). Electrospinning is a simple and versatile technique for producing ultra-fine fibres from polymeric solution or melt using electric charge (Chronakis, 2005). It is a very cost-effective technique compared to other nanomaterial synthesis technique such as chemical vapour deposition. This topic will be discussed in more detail in Chapter 2.

In some studies, carbon nanotubes (CNT) were added into the CNF in attempts to enhance the mechanical and electrical properties of CNF. CNT is known as allotropes of carbon with cylindrical molecular structure of carbon atoms with a length to diameter ratio larger than 1,000,000 (Hirlekar et al., 2009). Due to the very high surface area, stiffness, strength, and resilience, CNT offers novel properties that are highly potential for numerous applications in nanotechnology (Hirlekar et al., 2009). A study by Pasanen et al. (2009) reported that inclusion of CNTs in polymers would improve the polymer's tensile strength, elastic modulus, chemical resistance, and thermal shrinkage during stabilisation and carbonisation process. However, to the best of the author's knowledge, there is limited information available regarding electrical properties of CNT-filled CNF especially in terms of electrical conductivity, relative permittivity, and loss tangent.

The focus of this study is to fabricate and characterise CNF and CNT-filled CNF electrospun fibre membranes. Pure PAN and CNT-filled PAN precursor solutions were prepared prior to electrospinning process. After the electrospinning process, the as spun PAN and CNT-filled PAN nanofibre underwent a thermochemical process at elevated temperature to transform it into CNF and CNT-filled CNF. Characterisation of the membrane will be carried out to determine the physical, chemical, and electrical properties of the membrane. The main hypothesis of this study is that the inclusion of CNT into CNF would improve the electrical properties of the membrane. The knowledge that will be gained from this study is important to extend the application of electrospun nanofibre in electronic applications.

1.2 Problem statement

A proper selection of material for electronic applications such as sensors is critical to make sure that the product has the desired range of capabilities in terms of sensitivity, selectivity, and reliability (Luoh and Hahn, 2006). In general, sensor materials should possess characteristics such as good electrical conductivity and high effective surface area. In this regard, the very high surface area and high porosity of electrospun nanofibre membranes are the main attractive attributes that make electrospun nanofibre membranes as highly potential candidates for ultrasensitive sensors and other nano-sensing applications (Ding et al., 2010). A significant amount of effort has been dedicated by researchers in studying the effects of high surface area of the material on the performance of the sensors (Llobet, 2013). One of the popular choice of materials from these studies were CNF and CNT-filled CNF. To an extent, the physical, chemical and mechanical properties of the CNF and CNT-filled CNF are well characterised (Ra et al., 2005, Guo et al., 2010, Qiao et al., 2011, Chien et al., 2014, Rubia et al., 2014, Kaur et al., 2016). However, there were few studies dedicated on the electrical properties especially in terms of conductivity, permittivity and loss tangent of the electrospun CNF, and their relationships with physical and chemical properties of the fibres. Therefore, a comprehensive study is required to give an insight knowledge about the topic.

1.3 Research objectives

The objectives of the research are as follows:

1. To determine the optimum electrospinning parameters of polyacrylonitrile precursor material.
2. To evaluate the morphological, chemical, and electrical properties of carbon nanofibre (CNF) with different pyrolysis parameters.
3. To characterise the morphological, chemical, and electrical properties CNF with different weight percentage of multi walled carbon nanotube (MWCNT).

1.4 Scope of research

The scopes of the research are as follows:

1. Polyacrylonitrile (PAN) polymer was chosen as the precursor material and dimethylformamide (DMF) as a solvent.
2. PAN electrospun nanofibre were produced using electrospinning process.
3. The range selection of electrospinning parameters for electrospinning distance was 5 cm to 30 cm and applied voltage was 5 kV to 20 kV.
4. The range selection of pyrolysis parameters for carbonisation temperature was 800 ºC, 1000 ºC and 1200 ºC with heating rate 3 ºC/min and 5 ºC/min in a nitrogen filled furnace.
5. The physical and morphological characteristics of the nanofibre were characterised using scanning electron microscopy (SEM) and transmission electron microscope (TEM).
6. The fibre diameter of electrospun nanofibre before and after pyrolysis process were measured by using Image J software.