SILVER NANOPARTICLES / CARBOXYMETHYL-CELLULOSE NANOFIBERS SYNTHESIZED BY ELECTROSPINNING TECHNIQUE

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Applied Science (Honours) Material Technology

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SEPTEMBER 2016

SUPERVISORS' DECLARATION

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DEDICATION

Dedicated to my beloved parents, Faridah Binti Ismail and Mohamad Rani Bin Mat, siblings, supervisor, lecturers and all my friends. You are my inspiration.

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.

ABSTRACT

Demand on nanotechnologies product initiate to many studies and investigations to produce better applications. In this research, the polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC) were synthesized successfully to fabricated a nanofiber by using electrospinning method. The ratio of CMC and PVA is 3:7 with the concentration of 1.5 wt% and 11 wt% respectively. It was then blended into different volume of AgNPs. The surface morphology of CMC/PVA incorporated with AgNPs at 6.67 v/v%, 13.33 v/v% and 20 v/v% were observed under field emission scanning electron microscope shown uniform and smooth nanofibers with average diameter of 126.90 ± 27.56, 126.90 ± 27.50, 141.26 ± 25.66 and 114.86 ± 23.79 nm respectively. Thermo gravimetric analysis discovered the higher weight loss of 88.12 % in fiber containing 6.67 v/v% of AgNPs. Meanwhile, FTIR result demonstrated that all nanofibers presented O-H group in range of 3300 - 3600 cm^{-1} and C-O stretching vibrations in range of 1055 - 1138 cm^{-1}. All peaks showed the shiffness to the left as the amount of AgNPs were increased. Hence, the study on the properties of CMC/PVA incorporated with AgNPs nanofibers might be suitable as reference for various applications such as tissue engineering, drug delivery, water filter, sensors and energy storage.

ABSTRAK

Permintaan terhadap produk teknologi nano mendorong kepada banyak kajian dan penyelidikan untuk menghasilkan aplikasi yang lebih baik. Dalam kajian ini, PVA dan CMC berjaya disebatikan untuk menghasilkan serat nano menggunakan teknik pusingan elektro. Nisbah CMC dan PVA adalah 3:7 dengan kepekatan masing-masing sebanyak 1.5 wt% dan 11 wt%. Ia kemudiannya dicampur dengan AgNPs mengikut isipadu yang berbeza. Ciri-ciri morfologi CMC/PVA mengandungi AgNPs pada 6.67 v/v%, 13.33 v/v% dan 20 v/v% dilihat menggunakan pelepasan bidang imbasan mikroskop elektron menunjukkan serat nano yang seragam dan rata dengan garis pusat purata yang diperoleh setiap satu adalah 126.90 ± 27.56 , 126.90 ± 27.50, 141.26 ± 25.66 dan 114.86 ± 23.79 nm. Mesin analisis termogravimetri menunjukkan kadar kehilangan berat tertinggi iaitu sebanyak 88.12 % untuk serat mengandungi 6.67 v/v% AgNPs. Manakala, keputusan FTIR menunjukkan kehadiran kumpulan fungsi O-H dalam semua serat lebih kurang pada 3300 - 3600 cm^{-1} dan getaran regangan oleh C-O dalam anggaran 1055 - 1138 cm^{-1}. Maka, penyelidikan terhadap ciri-ciri serat nano CMC / PVA digabungkan dengan AgNPs mungkin dapat diaplikasikan dalam pelbagai kegunaan seperti kejuruteraan tisu, pengangkutan dadah, penapisan air, pengesan dan penyimpanan tenaga.

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LIST OF SYMBOLS

~	-	approximately
%	-	percent
µ	-	micron (10^{-6})
ml	-	millilitre
^{o}C	-	degree celcius
mg	-	milligrams
v/v %	-	volume per volume percentage
cm	-	centimeters

LIST OF ABBREVIATIONS

PVA	-	Polyvinyl alcohol
CMC	-	Carboxymethyl cellulose
AgNPs	-	Silver nanoparticles
ES	-	Electrospinning
ATR-FTIR	-	Attenuated total reflectance-fourier transform Infrared spectroscopy
TGA	-	Thermogravimetric analysis
SEM	-	Scanning electron microscope
FESEM	-	Field emission scanning electron microscope
UV-VIS	-	Ultraviolet- visible spectrophotometer

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE PROBLEM

Cellulose is one of the most abundant biopolymer source in Malaysia and it can be extracted by low cost method (Miao et al., 2016). It is composed of a long chain of glucose molecules, normally known as polysaccharide. These chains are bonded by hydrogen bond and arranged together in parallel arrays to form cellulose microfibrils (Miao et al., 2016). Thus, the structure form as crystalline. The number of chains present in microfibrils gave effect to the complexity of the structure (Thomas et al., 2013). There has increased interest toward cellulose due to its renewability and stability (Miao et al., 2016). Furthermore, it has been reported that cellulose materials are nontoxicity and biodegradability (Gong et al., 2009). Thus, it can be used in many applications such as tissue engineering, drug delivery, water filter, sensors and energy storage.

Carboxymethyl cellulose (CMC) contains a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups, hence shows amphiphilic characteristics (Su et. al., 2010). It's becoming one of natural water-soluble cellulose derivatives that have no harmful effects on human health. It is widely used in stabilizing food, emulsifier as well as to control enzyme activities (Su et al., 2010). CMC can be obtained by synthetization of alkali-catalyzed reaction of cellulose with chloroacetic acid. The polar carboxyl group present in the structure make it soluble and chemically reactive.

Nowadays, there are lots of technology that have been invented in producing nanofibers material such as phase separation, template and electrospinning method.

Fibrous materials have many advantages compared to bulk counterpart due to their present in high area/volume ratio and tunable porosity (Martinez et al., 2016). Among others method, electrospinning method has gained many attention among researcher due to its ability to get smooth nanofibers. It has been used to produce considerable amount of nanofibrous materials based on natural and synthetic polymers with fiber morphology and specific physicochemical properties (Martinez et al. 2016). There are 3 major parameters covered by electrospinning method which are (i) solution parameters (viscosity, surface tension, conductivity/surface charge density), (ii) ambient parameters (humidity and temperature), and (iii) process parameters (voltage, flow rate, collectors and also the distance between collector and the tip of the syringe). (Li & Wang, 2013) . Each of the parameter give a significant affect to the result of morphology and diameters of the fibers.

This research has proposed to study the effect of silver nanoparticles on CMC nanofibers material based on green chemistry approach by using water as the only solvent. Products consist of silver nanoparticles have been approved by accredited agencies including the U. S. FDA, U. S. EPA, SIAA of Japan, Korea's Testing and Research Institute for Chemical Industry and FITI Testing & Research Institute. From the past study, they are using chemical reduction methods which are expensive, hazardous to environment and required harmful UV light or microwave radiation during the preparation (Meng, 2015). Hence, further research should be conducted with more eco-friendly method. The advantages of green chemistry approach include cost saving, reduce consumption of energy, decrease reaction time and considerable reduction time in reactor size (Jeon et al., 2005). Thus, green chemistry approach has been practiced during this experiment by concerned the matters on the surrounding issues. Then, the properties of the fiber are characterized by using SEM, FESEM, ATR- FTIR, UV-vis, and TGA.

1.2 STATEMENT OF THE PROBLEM

Demand on non-toxicity, cost effective and safe polymeric materials for various industrial applications.

1.3 OBJECTIVES OF THE STUDY

The objectives of this study are:

i. To study the effect of Silver nanoparticles in Carboxymethyl - Cellulose nanofibers.
ii. To identify physical and thermal properties of fabricated nanofibers.

1.4 SCOPE OF STUDY

To achieve first objective, the scope of study are:

i. To optimize the parameters of electrospinning including solution parameters, process parameters and ambient parameters.
ii. To synthesized varied amount of silver nanoparticles at constant concentration of Carboxymethyl-cellulose.

To achieve second objective, the scope of study are:

i. To observe the crystalline and morphological features of AgNPs/CMC/PVA nanofibers by using scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM).
ii. To study the thermal properties of AgNPs/CMC/PVA nanofibers by using thermogravimetric analysis (TGA).
iii. To identify the existed bond of AgNPs/CMC/PVA by using Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR).
iv. To obtain the particles size distribution of AgNPs/CMC/PVA by using Ultraviolet-Visible Spectroscopy (UV-Vis).

CHAPTER 2

LITERATURE REVIEW

2.1 BIOMATERIAL

Biomaterial is defined as a substance of material that is modified alone or as part of complex system by using direct or controlled by the interaction with components of living systems (Goldberg et al. 2011). It undergo therapeutic or diagnostic procedure. It has widely used in clinical practices. Scope of area related cover by biomaterials such as cancer diagnosis and therapy, implantable devices, drug delivery systems, gene vectors, bionanotechnology and tissue engineering.

2.1.1 Classification of Bionanotechnology

Bionanotechnology can be classified into one, two or three dimensions of nanoparticles. It is covered biological, biomedical and medical applications. Micro and nano technology tools had been used for sensoring and therapeutics and also had been implied in drug delivery devices for targeted therapy (Azmath et al. 2016). Artificial organ and devices also had been developed using fabrication and scaffold techniques by micro and nano structured surfaces and tissue engineering.

2.1.2 Carboxymethyl Cellulose (CMC)

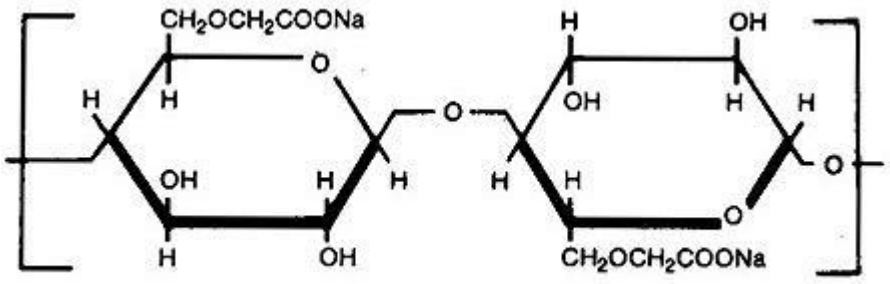

Figure 2.1. The molecule structure of CMC.
Source: Purchased from (ARCOS Organics, New Jersey, USA)

Carboxymethyl-cellulose is a water soluble polymer that is derived from wood or cotton cellulose (wall of plants) (Thomas et al., 2013). As the carboxymethyl group introduced into the cellulose backbone forming anionic cellulose molecules hydrate which can be dissolved in water without further process (Thomas et al., 2013). CMC can act as a viscosity modifier or thickener, and also can be used to stabilize emulsion in food production products such as ice cream and cheese (Thomas et al., 2013). It is commercially been used in toiletries, paint, paper products as well as detergent. Furthermore, CMC is not absorbed or digested, so it might be included in with "dietary fiber" on food labels. In food additive types compared to CMC, olestra (olean) can cause diarrhea, flatulence and abdominal cramps.

2.1.3 Silver Nitrate

Silver nanoparticles is low cost and high potential applications (Naraginti & Sivakumar, 2014). It can be extended into broad spectrum of applications as an inorganic hybrid nanocomposite materials (Pencheva et al., 2012). Previously, AgNPs said to be good in wound healing, better for cosmetic appearance and scarless healing when it was tested to animal model (Pencheva et al., 2012).

2.1.4 Polyvinyl alcohol (PVA)

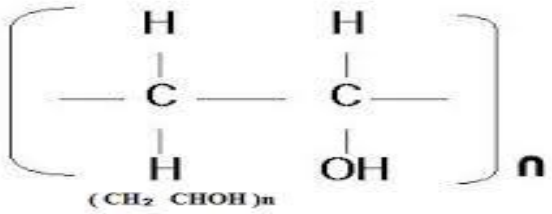

Figure 2.2. The molecule structure of PVA.

Source: Purchased from (ARCOS Organics, New Jersey, USA)

The polymerization of vinyl acetate to poly (vinyl acetate) undergo hydrolysis process to form polyvinyl alcohol (PVA). It has excellent film forming, adhesive properties, stabilizer (Pencheva et al., 2012), emulsifying and an atactic material that exhibits crystallinity. It is nontoxic and can be degradable easily. In industries, PVA has certain grade which effect the degree of hydrolysis as well as its chemical properties, solubility, and cystallizability (Hassan & Peppas, 2000). PVA with high degree of hydrolysis have low solubility in water and it is more difficult to crystallize while a lower degree of hydrolysis will promote polymerization stability, improved water sensitivity, and formed decrease size particle.

2.2 SYNTHESIS OF NANOFIBERS

2.2.1 Electrospinning method

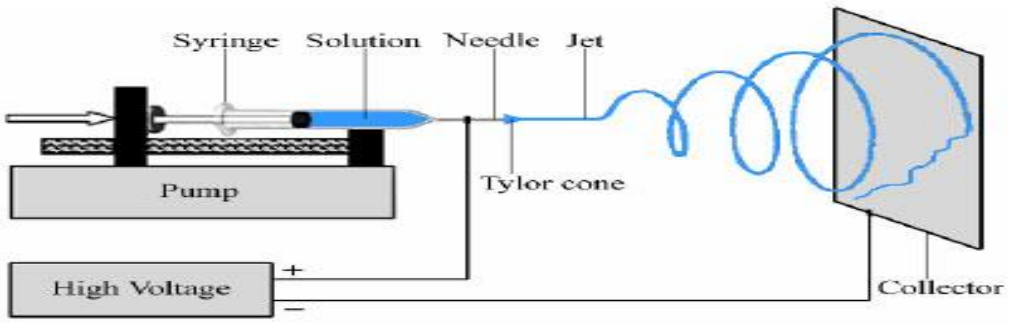

Figure 2.3. Set up of electrospinning

Source: Retrieved from (Braz, 2009)

Electrospinning is a simple and cost-effective method that can produce ultrafine solid and continuous fibers in nanoscale of 1 to 100 nm. It is a process of producing fibers conducted at room temperature and compatible to be implied in many applications. Basically, the system of the electrospinning consist of three major components which are high voltage power supply, a spinneret and a grounded collecting plate. There are two electrospinning set up which are horizontal and vertical. An appropriate parameters such as voltage supply, feed rate, tip-to-collector distance, and rotation speed should be considered to produce ultrafine fibers (Ziabari et al., 2009). In this experiment, green chemistry approach was proposed using water as the only solvent for fiber fabrication using electrospinning method. It is less harm, thus reducing the risk of chemical effect towards environment.

2.3 CHARACTERIZATION TECHNIQUE

There are many types of characterization instrument to measure different properties of silver nanoparticles/carboxymethyl cellulose nanofibers such as; SEM, FESEM, TEM, ATR-FTIR, UV-VIS and TGA. These instruments are used to measure the physical and thermal properties of fabricated nanofibers.

2.3.1 Scanning Electron Microscope (SEM)

Characterization by Scanning Electron Microscope (SEM) examined topography and composition. Non-conductive material or sample must be coated to avoid electron charging and image degradation. Thin coating usually by carbon or titanium. Electron gun at the top produce a high concentrated electrons beam which is directed to the specimen under examination. Then, the Thermionic guns heat the filament to accelerate the electron with the voltage between 1 kV to 30 kV. The second gun, Field emission gun drift electrons away from their atoms by generating a strong electrical field. Vacuum chamber needed to prevent electron beam and there are series of lenses within it. These lenses function as to direct the electrons towards the specimen in order to maximize efficiency of the penetrant. As the acceleration of electrons increase, the power of magnification also increase. Later, electrons beam pass through the body of microscope and small particles could deflect the electrons onto the specimen known as an incident

beam. It lastly emits X-rays and electrons which is primary backscattered electrons and secondary electrons (ZEISS Evo50).

2.3.2 Field Emission Scanning Electron Microscope (FESEM)

Compared to conventional SEM, it can produce six times better image with less electrostatically distorted. The basic principle of it is, field emission cathode in the electron gun with narrow probing beams either at low or high electron energy can improve resolution for highest magnification. FESEM enable to examine smaller area of contamination spot at a compatible electron accelerating voltage with energy dispersion spectroscopy, it can reduce penetration of low kinetic energy electrons and can produce high quality image as it can minimize the electric charging and damage of the sample. The best part of this is, no requirement to placing the conducting coating on insulating materials (JEOL, JSM- 7800F).

2.3.3 Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

ATR-FTIR was using electromagnetic radiation which presented with wavelength as x-axis. It was checking the bond exist in sample by examined functional group region to determine in which group it might be present at a solid/surface interface. In spectra organic, there are two division of areas which are the functional group region and fingerprint region. Basically, the functional group region indicated peak region resembles the characteristic of specific bonds and specific functional group only. While in fingerprint region, it arise from complex deformations of the molecules resulting from molecular symmetry or combination bands arising from multiple bond deforming. The advantages of this characterization technique are multiple scans can be conducted to improve signal to noise ratio and data obtained from the computer software can be corrected to the baseline, edit peaks formed or otherwise can correct the limitations of the sample (Pelkin Elmer).

2.3.4 Ultraviolet-visible Spectrophotometer (UV-vis)

UV-Vis is one of the technique used to check the presence of nanoparticle in the sample. It has high possibility to observe small particle in the presence of large one. The sample need to be dissolved well. To obtain the result, data acquires from the UV to the near IR. Small footprint needed for easy transport and storage. Furthermore, increase of sample throughput with the integrated 6-cell charger. To make the result more precise, there must be in controlled thermosetting options with circulating water and Petlier cooling. In addition, samples can be tested with a variety of optional holders for test-tubes, long path cuvettes and filters. Adding a sipper accessory may help in sample handling easily. The features for local control are acquire, display, manipulate and save scanning. It is fixed in wavelength, kinetic and data concentration as well. Board library can automatically save the methods and data of sample testing.

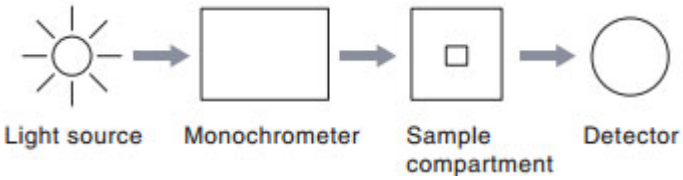

Figure 2.4. Schematic diagram of a single UV-vis**.**
Source: Retrieved from **(**Shimadzu, UV-2600)

As shown in figure 2.3, the sample can exposed to monochromatic light but there are instruments in which white light can pass through the sample before being passed into the spectrometer. This single monochromator providing low noise performance across a wide wavelength range (up to 1400 nm). This method is employed high speed photometry set up that use array detectors in it working. Sources of light that used in this having a properties of high stability over time, long service life and low cost. Deuterium lamps are used for the ultraviolet region. **(**Shimadzu, UV-2600).

2.3.5 Thermogravimetric Analyzer (TGA)

In this project, TGA testing for study the thermal properties was carried out using Mettler Toledo-TGA/DSC1. This instrument has a micro-balance and a thermocouple sensor to simultaneously measures heat flow in addition to weight change as a function of temperature. It has sensitivity of microgram resolution which approximately 2 microgram over the whole measurement range. High efficiency automation, the load up to 32 samples throughput. Furthermore, it has broad temperature scale which can analyze samples from ambient to 1000 °C. It is able to detect thermal or heat flow measurement by only using single thermocouple. Built-in mass controller which may consist of hydrogen gas is important in order to control the atmosphere around the sample and user interaction is not necessary when starting an experiment (Mettler Toledo).

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CHAPTER 3

RESEARCH METHODOLOGY

3.1 INTRODUCTION

Poly (vinyl alcohol) with molecular weight 95000 were purchased from ACROS Organics, New Jersey, USA. The carboxymethyl cellulose (CMC) with molecular weight 250000 were purchased from ACROS Organics, New Jersey, USA. The silver nitrate ($AgNO_3$) were purchased from R & M Marketing, Essex, U.K. All the raw materials employed in this synthesis process had been through of analytical reagent grade. There is no further purification. All the solutions were prepared by using millipore water.

3.1.1 Synthesis of CMC/PVA solutions.

The CMC solution with a concentration of 1.5 wt% was prepared by dissolving 7.5 g of CMC powder in 500 ml of millipore water for 48 hours at room temperature until a clear solution is obtain with a slight increase in viscosity. PVA solution of 11 wt% was prepared by dissolving 55 g of PVA granules in 500 ml of millipore water and stirring at 80 °C for 7 days.

Both solutions was stirred continuously at room temperature to ensure complete mixing and eventually obtain a homogeneous solution. This is also to ensure that air bubbles were completely removed from the solution. Then, CMC was blended in PVA solution with 3 different weight ratios of CMC/PVA, which are 50:50, 40:60 and 30:70 and stirred overnight to get a homogeneous mixture for electrospinning. The best weight ratio were used in further synthesization.

3.1.2 Synthesis of CMC/PVA/silver nanoparticles

Silver Nitrate, $AgNO_3$ was dissolved in millipore water to prepare solution with the concentration of 0.24 mg/mL. Then, $AgNO_3$ solution was added to the CMC solution (6.67 v/v%, 13.33 v/v%, 20 v/v%) with constant stirring at 75 ^oC for 2 hours, in a dark environment. The CMC solution was acquired brown colour, indicating the reduction of Ag^+ to Ag^0. The blend solutions of CMC/AgNPs were stirred overnight to get homogeneous solutions. Homogenous CMC/AgNPs then were mixed with PVA and it was stirred overnight with constant stirred.

3.1.3 Electrospinning method

The ratio of 30:70 has been furthered since the tested ratio of 50:50 and 40:60 of CMC/PVA could not fabricated the nanofibers. The mixture of CMC/PVA with ratio 30:70 was filled in a syringe fitted with a blunt steel needle of 0.8 mm inner diameter and flow rate of 0.06 ml/h. The applied voltage used 25 kV. The electrospun nanofibers were collected using a rotating drum collector wrapped with aluminium foil at the distance of 6.4 cm from tip-to-collector. The collected electrospun nanofibers were stored in desiccators for further use. The same parameters and conditions applied to the PVA/CMC-AgNPs solutions.

3.1.4 Sample Characterizations

The characterization instruments to measure different properties of nanofibers are; SEM, FESEM, ATR-FTIR, UV-VIS and TGA. These instruments are used to measure the physical and thermal properties of fabricated nanofibers.

3.1.4.1 Scanning Electron Microscope (SEM)

In this proposed research, SEM- CARL ZEISS Evo50 brand used for imaging of sample surfaces at high magnification and resolution. It provided morphological features likes, surface morphology, structure, topology and elemental mapping view of the sample. The sample was coated with platinum in vacuum

.

Figure 3.1. Scanning Electron Microscope.
Source: Purchased from (ZEISS EVO50)

3.1.4.2 Field Emission Scanning Electron Microscope (FESEM)

FESEM was used to checking crystalline and morphological features with better image. This result will support the images obtained from SEM. This characterization methods were used to the fiber samples with the silver nitrate content. The spartial resolution at 1nm is achievable for solid sample at magnification up to 500K (JEOL, JSM-7800F). The samples were coated with platinum in vacuum.

Figure 3.2. Field Emission Scanning Electron Microscope.
Source: Purchased from (JEOL JSM-7800F)

3.1.4.3 Attenuated Total Reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

FTIR is the spectroscopic method used for characterizing organic and inorganic compound. It shown the present of bond for the tested sample. The scanned region is 700 – 4000 cm^{-1}, at resolution of 4 cm^{-1}. IR spectra were recorded on Perkin Elmer Spectrum 100 FTIR with Pike ATR Spectrum 100 FT-IR Perkin Elmer FT-IR complete system with computer and LED monitor.

Figure 3.3. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy. Source: Purchased from (Pelkin Elmer)

3.1.4.4 Ultraviolet-Visible Spectroscopy (UV-Vis)

In this project, UV-vis spectrophotometer of Shimadzu brand, model UV-2600 was used to obtain absorbance at the range of 200 to 900 nm. Confirmation of sample formation were assisted by the plasmon resonance (Abou et al., 2010). It provided high and strong illumination from the UV to the near IR region and having optional integrating sphere which can be extended to high wavelength (Shimadzu, UV-2600).

Assisted with validation software which connected to computer for easy checking of inspection and high accuracy of data. This spectrophotometer can be used in wide range of applications and can obtain result easily.

Figure 3.4. Ultraviolet-Visible Spectrophotometer.
Source: Purchased from (Shimadzu)

3.1.4.5 Thermogravimetric analyzer (TGA)

In this project, TGA testing for study the thermal properties was carried out using Mettler Toledo-TGA/DSC1. This instrument has a micro-balance and a thermocouple sensor to simultaneously measures heat flow in addition to weight change as a function of temperature. It has sensitivity of microgram resolution which approximately 2 microgram over the whole measurement range. High efficiency automation, the load up to 32 samples throughput. Furthermore, it has broad temperature scale which can analyze samples from ambient to 1000 ^{o}C. It is able to detect thermal or heat flow measurement by only using single thermocouple. Built-in mass controller which may consist of hydrogen gas is important in order to control the atmosphere around the sample and user interaction is not necessary when starting an experiment (Mettler Toledo).

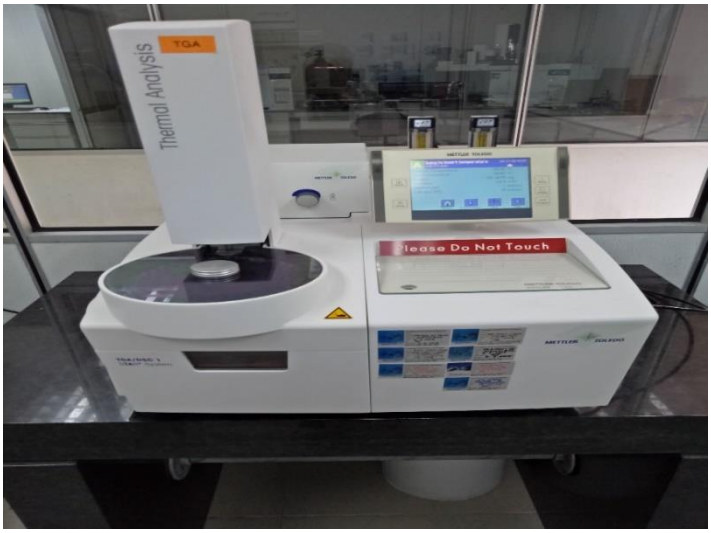


Figure 3.5. Thermogravimetric analyzer.

Source: Purchased from (Mettler-Toledo)

CHAPTER 4

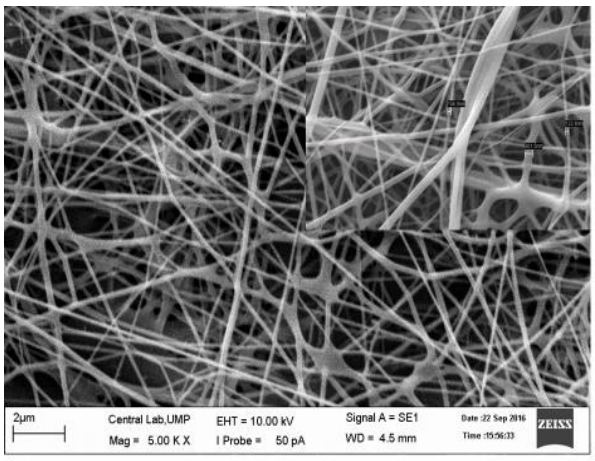
RESULT AND DISCUSSION

4.1 INTRODUCTION

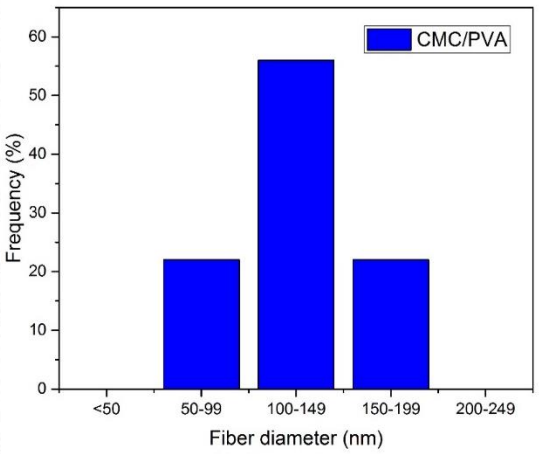
In this chapter, the morphology, thermal and functional group of CMC/PVA and CMC/PVA/AgNPs were further analyzed and discussed by using SEM, FESEM, UV-VIS, ATR-FTIR and TGA. These properties study would be helpful to presume the physical features of nanofibers for suitable application

4.2 SYNTHESIS AND CHARACTERIZATION

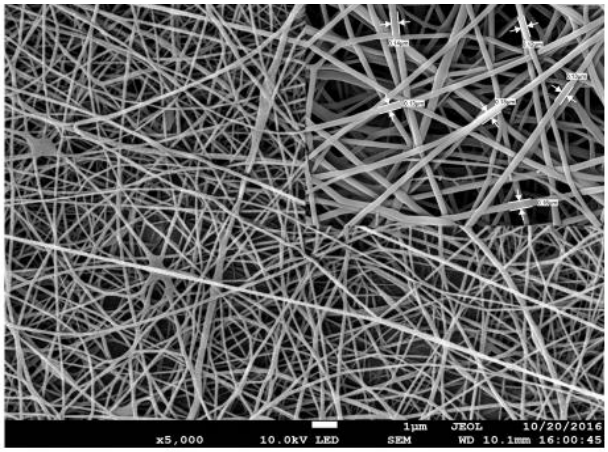
4.2.1 Morphology analysis

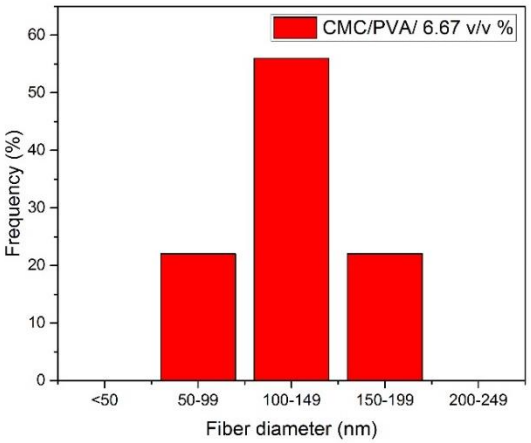


(a)

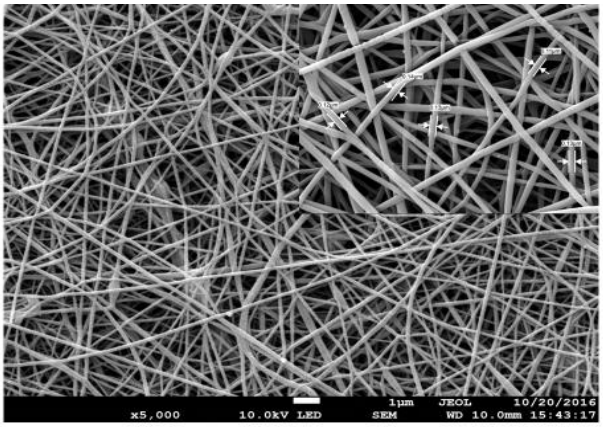


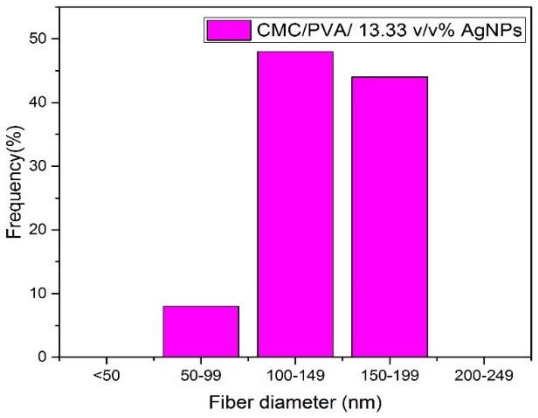
(b)



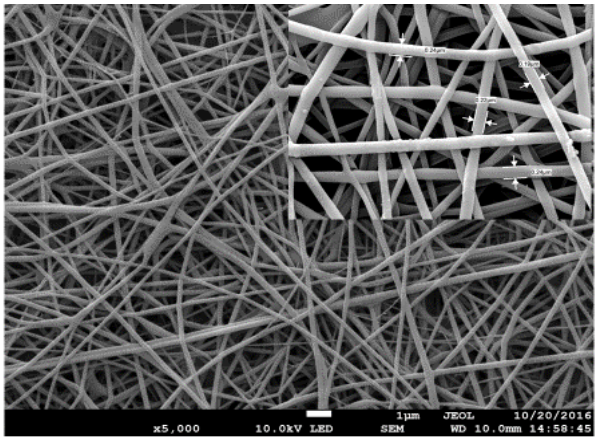


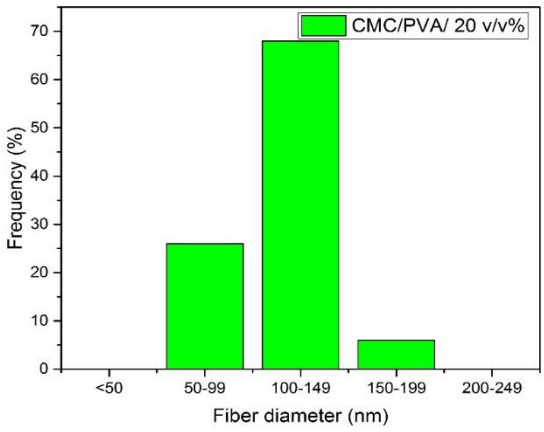
(c) (d)





(e) (f)





(g) (h)

Figure 4.1. Images and diameter distribution of electrospun CMC/PVA nanofibers with different concentration of AgNPs: (a,b) pure CMC/PVA, (c,d) 6.67 v/v%, (e,f) 13.33 v/v%, (g,h) 20 v/v%

Table 4.1
Average diameter distribution of CMC/PVA and CMC/PVA/AgNPs nanofibers

Sample	Average diameter (nm)
CMC/PVA	126.90 ± 27.56
CMC/PVA/ 6.67 v/v% AgNPs	126.90 ± 27.50
CMC/PVA/ 13.33 v/v% AgNPs	141.26 ± 25.66
CMC/PVA/ 20 v/v% AgNPs	114.86 ± 23.79

Figure 4.1 shows the SEM/FESEM images of CMC/PVA and CMC/PVA at different concentration of AgNPs; (c) 6.67 v/v%, (e) 13.33 v/v%, (g) 20 v/v%. The image revealed uniform, porous, beadless and nanoscaled fibrous structure in the range of 114 - 141 nm. Nanofiber mats of CMC/PVA/ 20 v/v% showed the smallest average diameter if compared to others. This might be due to the additional of AgNPs at optimum concentration which leads to higher surface area of the fibers.

The measurement of nanofibers diameter is very important to estimate the possible applications that most suitable for the fibers. For example, the average diameters of ~200 nm is suitable for skin tissue engineering while for water filter application, it will at average diameter less than 100 nm (Zulkifli et al., 2014).

4.2.2 UV-Vis analysis

UV-Vis was conducted to verify the present of silver nanoparticles in the prepared solution. Silver nanoparticles absorb radiation in the visible region of the electromagnetic spectrum due to the excitation of surface plasmon vibrations (Lv et al., 2013). This surface plasmon resonance arises due to the free oscillating electron on the metal nanoparticles which absorb the electromagnetic radiation from particular energy levels (Zulkifli et al., 2014). Changes in color's solution containing silver nitrate from clear solution to brown indicates the present of silver nanoparticles. The intensity of colors were differ with the amount of silver nanoparticles added into the CMC.

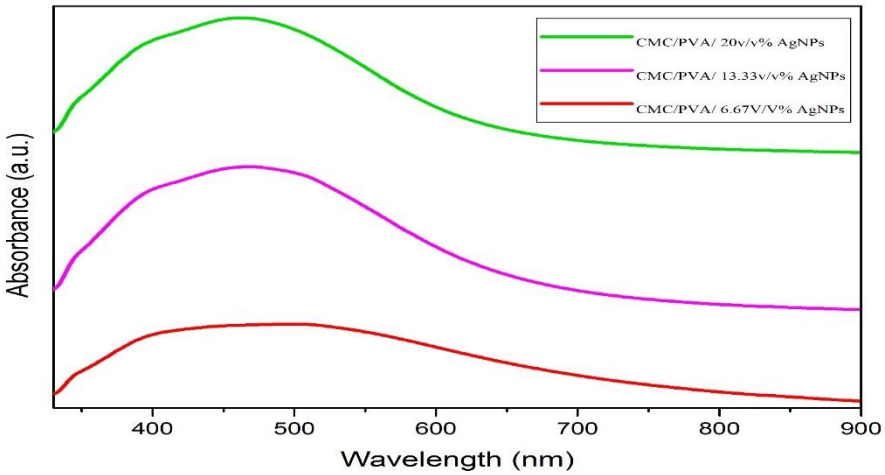


Figure 4.2. UV-Vis analysis of CMC/PVA with different concentration of AgNPs

Figure 4.2 showed peaks at 474.62 nm, 469.07 nm and 460.09 nm for CMC/PVA with 6.67, 13.33 and 20 v/v% respectively. The slight shift and sharpness of the absorption peak might effected by the change in the number and size of particles embedded in the sample (Sumitha et al., 2012). Hence, as the particles size become larger, the maximum absorption shift to longer wavelength and the peaks will become broaden.

4.2.3 ATR-FTIR spectra analysis

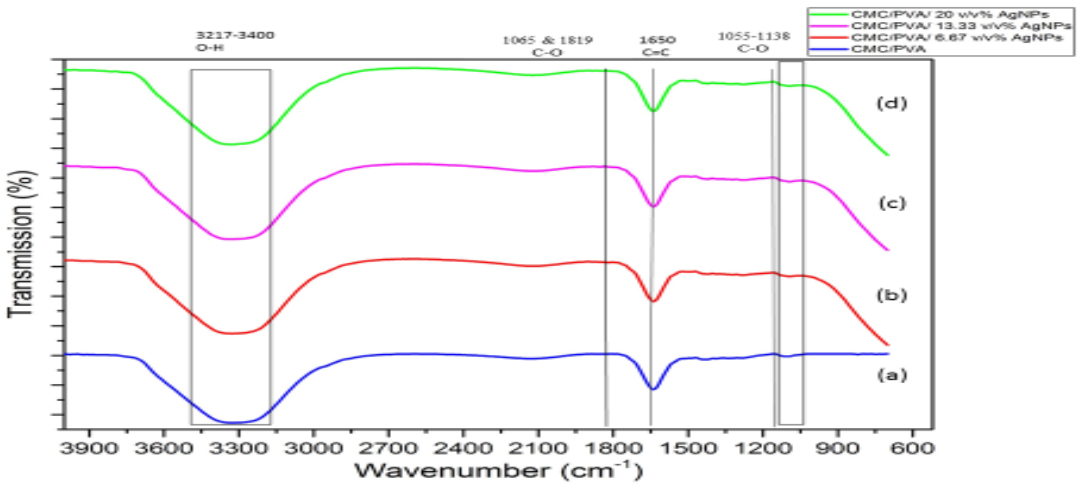


Figure 4.3. ATR-FTIR of electrospun CMC/PVA nanofibers with different concentration of AgNPs; (a) pure CMC/PVA, (b) 6.67 v/v% AgNPs, (c) 13.33 v/v% AgNPs, (d) 20 v/v% AgNPs

The ATR-FTIR spectra of CMC/PVA and CMC/PVA/AgNPs nanofibers are illustrated as in Figure 4.3. The broad peak at 3217 - 3400 cm^{-1} indicated stretching vibrations of the hydroxyl group due to the intramolecular and intermolecular hydrogen bonds of the OH group of CMC. ATR-FTIR spectra also revealed carbonyl strectch C=C at 1650 cm^{-1} of CMC. The absorption peaks at ~1819 cm^{-1} and ~1065 cm^{-1} shown the existence of carboxylate groups due to C-O stretching vibration. Lastly, the absorption peak observed from 1055 – 1138 cm^{-1} exhibited the C-O stretching vibrations which shown slightly shift to the left with decreased of AgNPs content.

4.2.4 Termogravimeter analysis

TGA measurement was conducted to the nanofiber mats to describe the weight loss behavior of the CMC/PVA and CMC/PVA/AgNPs. Thermal degredation behaviors of fiber examined by TGA as shown in Figure 4.4.

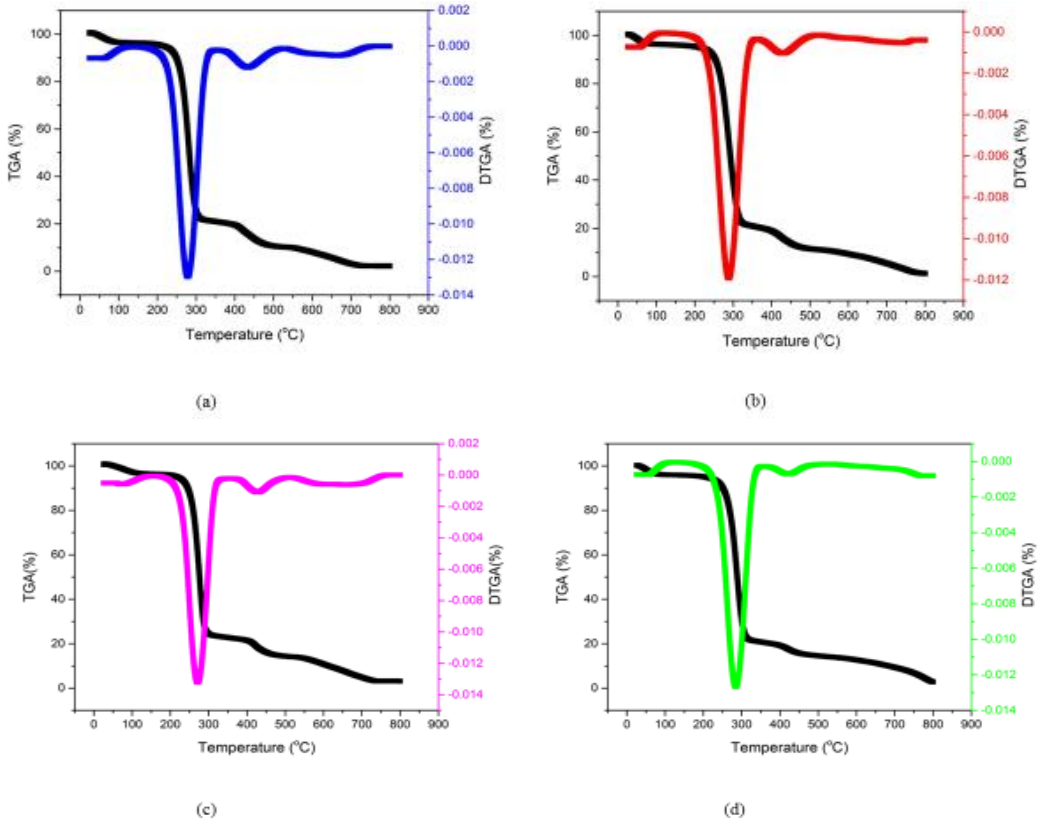


Figure 4.4. TGA and DTGA curve of electrospun CMC/PVA nanofibers with different concentration of AgNPs; (a) pure CMC/PVA, (b) 6.67 v/v% AgNPs, (c) 13.33 v/v% AgNPs, (d) 20 v/v% AgNPs

Table 4.2
TGA and DTGA for CMC/PVA and CMC/PVA/AgNPs nanofibers

Sample	Region of decomposition	Temperature (^{0}C)			Weight loss (%)	
		T_{start}	T_{end}	T_{peak}	Partial	Total
CMC/PVA	1st	20.56	151.29	72.08	3.01	88.02
	2nd	151.29	359.52	278.57	74.74	
	3rd	359.52	524.68	433.55	10.27	
CMC/PVA/ 6.67 v/v% AgNPs	1st	22.29	146.10	65.37	3.82	88.12
	2nd	146.10	357.79	290.69	74.23	
	3rd	357.79	498.92	430.09	10.07	
CMC/PVA/ 13.33 v/v% AgNPs	1st	20.56	156.49	91.13	5.22	86.21
	2nd	156.49	256.06	275.11	72.68	
	3rd	256.06	504.11	428.35	8.31	
CMC/PVA/ 20 v/v% AgNPs	1st	22.29	142.64	68.61	4.63	85.34
	2nd	142.64	356.06	288.96	74.07	
	3rd	356.06	500.64	419.70	6.64	

There are three major steps observed which distinguished in the diagram of mass loss (TGA %) during heating and these information was supported by the diagram of derivative mass loss (DTGA %). Table 4.2 shown the decomposition step and percentage of mass loss for the nanofiber mats. The 1st region indicated the presence of a thermal process due to weak physisorption of water or moisture evaporation (Zulkifli et al., 2014). Mass loss of this very 1st stage most likely to be resulted by the elimination of water which occurred at low temperature.

Figure 4.5 potrayed the decomposition process at the beginning stage (Dong et al., 2014). Allytic alcohols formed by elimination of water from structure in PVA molecular chains. Hence it easy to decomposed to form hydroxyl radical as shown in reaction 1. Then, this hydroxyl radical generated new free radical by the hydrogen abstracts as drawned in reaction 2. In reaction 3, the hydroxyl radicals are removed to form double bonds in PVA macromolecular chain. Hydroxyl radicals resulting from reaction 2 and 3 repeatedly take place, this call as unzipping type reaction of water molecule removal (Dong et al., 2014).

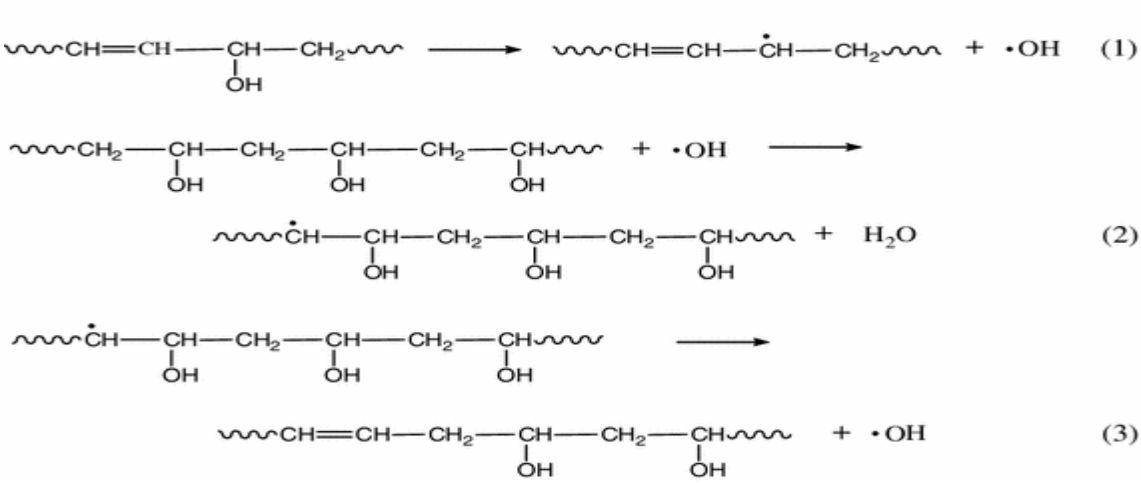


Figure 4.5. The decomposition reactions in the first step of mass loss
Source: Retrieved from (Dong et al., 2014)

One the other side, the most significant weight loss can be observed in 2nd decomposition region varying from 142.64 °C to 359.52 °C with maximum weight loss up to 74.74 %. In this 2nd region, verifying the existence of a chemical degradation process resulting from bond scissions of (i.e carbon-carbon bonds) in the polymeric bone and degradation of side chain PVA molecule and loss of CO_2 in the cellulose which is CMC (Mahmoud et al., 2011). Meanwhile, the weight loss in 3rd decomposition region, occurance can be monitored from 356.06 °C to 524.68 °C with weight loss reaching 10.27 %. The third weight loss was due to the by-products generated during thermal degradation process attributed to decomposition of the main chain (Holland & Hay, 2001).

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CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 INTRODUCTION

This chapter highlighted the conclusion and recommendation for further action of improvement of this study.

5.2 CONCLUSION

In this study, CMC/PVA with the ratio of 30:70 and the concentration of 1.5 wt% and 11 wt% respectively can fabricate nanofiber mats successfully. The characterization of the fibers were carried out by SEM (for pure CMC/PVA), FESEM (for CMC/PVA with additional of AgNPs), TGA, UV-VIS and ATR-FTIR. The surface morphology of electrospun CMC/PVA nanofibers of pure CMC/PVA and with different concentration of AgNPs; 6.67 v/v%, 13.33 v/v% and 20 v/v% shown average diameter distribution of 126.90 ± 27.56, 126.90 ± 27.50, 141.26 ± 25.66 and 114.86 ± 23.79 nm respectively. The highest weight loss of 88.12 % can be observed from nanofiber containing 6.67 v/v% of AgNPs. The broad peak of stretching vibration OH group of CMC presented at 3217 - 3400 cm^{-1}. Revealation of carbonyl strectch C=C at 1650 cm^{-1} and absorption peak observed from 1055 – 1138 cm^{-1} exhibited the C-O stretching vibrations shown slightly shift to the left with decreased of AgNPs content. The best performance of sample is CMC/PVA/ 20 v/v% AgNPs based on it morphology, chemical properties as well as thermal properties.

5.3 RECOMMENDATIONS FOR FUTURE RESEARCH

In this study, the characterization technique focused on surface morphology, chemical decomposition and thermal stability and decomposition. So, examination on the strength of fiber should be considered to more to determine whether it meet the requirements in the end-use application. In this research, it is focused on electrospinning technique only so, for future study might be can check it on difference techniques such as freeze-dry, gas forming and casting. Furthermore, the study of side effect of the materials used should be investigated especially when it comes to the application involving inner part of host's body.

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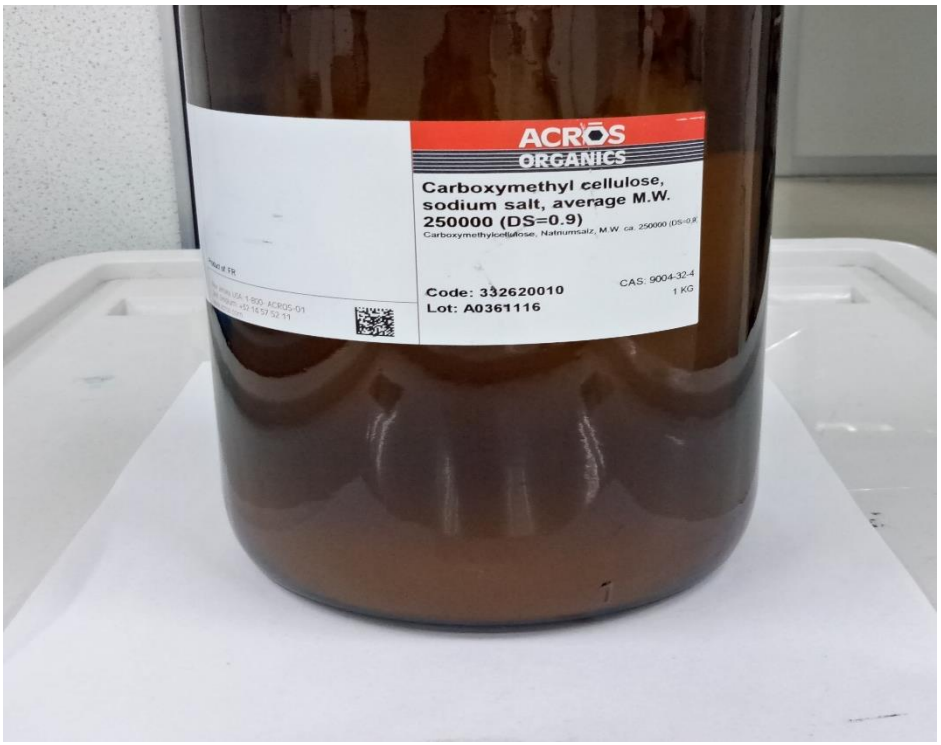
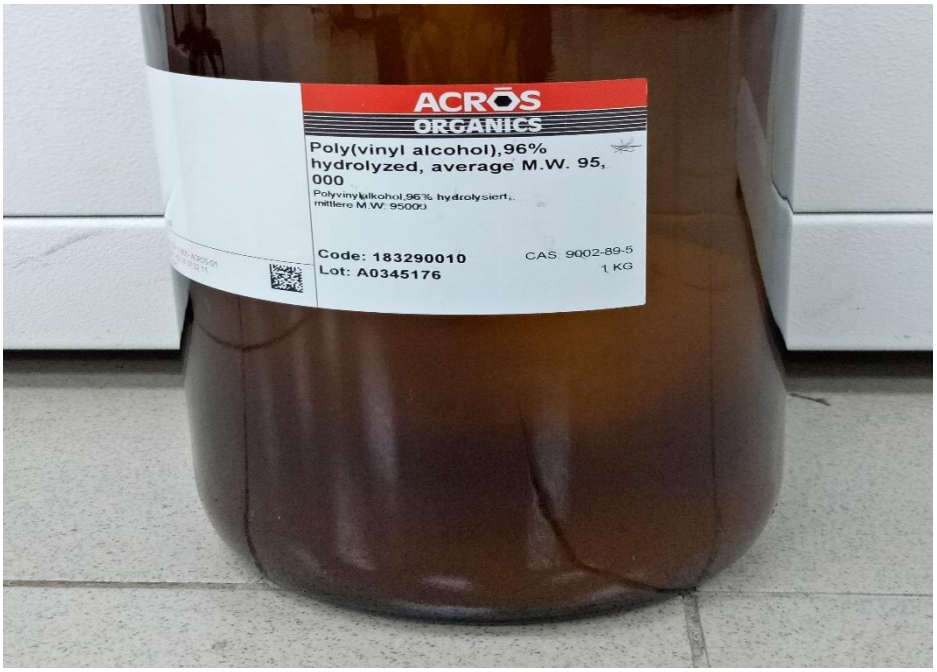
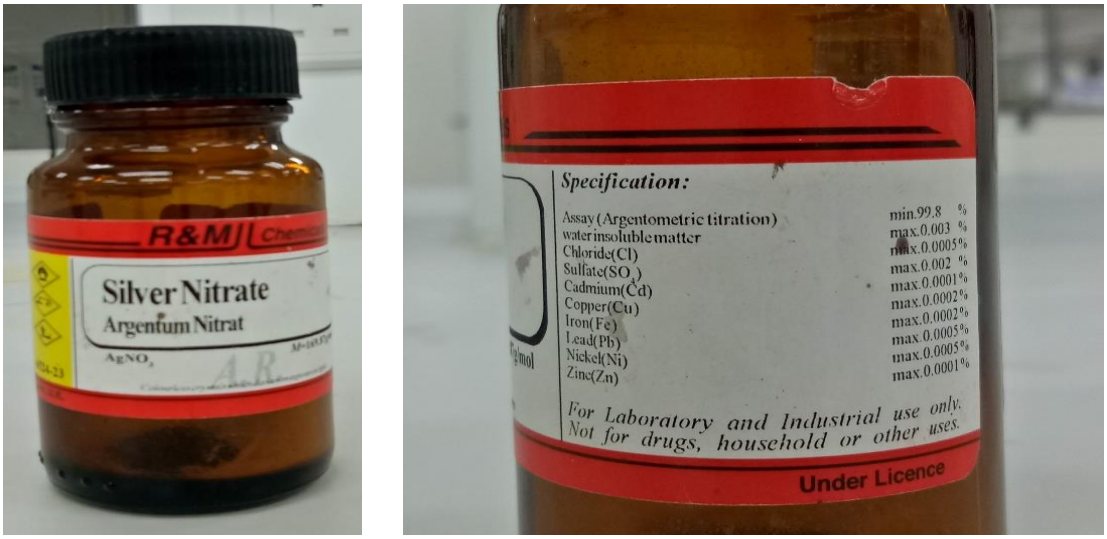
APPENDIX



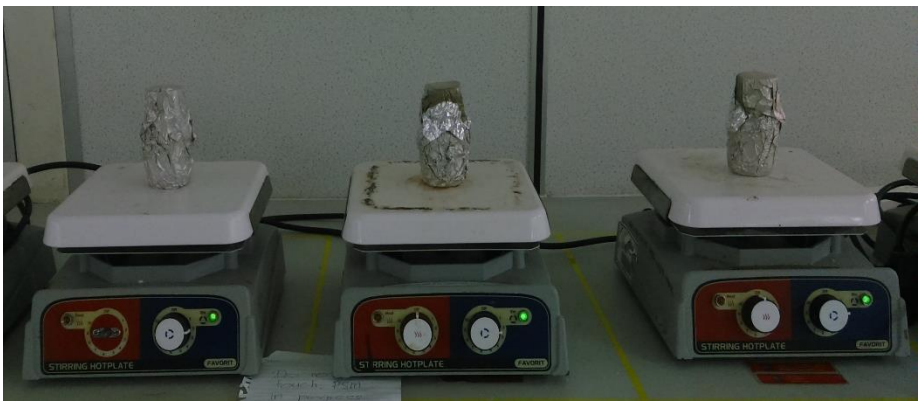
Carboxymethyl cellulose (CMC) with molecular weight 250000, ACROS Organics, New Jersey, USA.



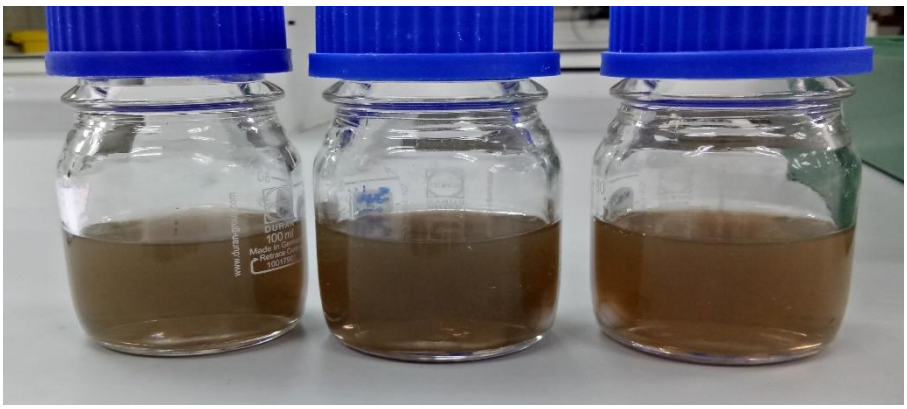
Poly (vinyl alcohol) with molecular weight 95000, ACROS Organics, New Jersey, USA.



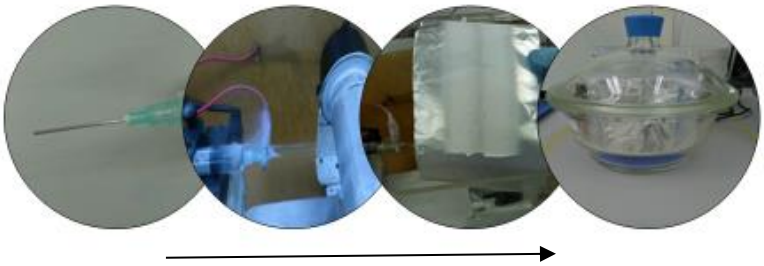
Silver nitrate ($AgNO_3$), R & M Marketing, Essex, U.K.



Photograph of CMC/AgNPs heated in dark environment



Photograph of CMC/AgNPs solution obtained at different concentration of AgNPs



Synthesis of nanofibers

Properties	CMC/PVA	CMC/ PVA/ 6.67 v/v% AgNPs	CMC/ PVA/ 13.33 v/v% AgNPs	CMC/ PVA/ 20 v/v% AgNPs
Quantity(mg)	0.9806	1.4199	0.7978	1.9428
Heating rate(°C/min)	10	10	10	10
Heating degree (°C)	800	800	800	800

Data of nanofibers sample for TGA and DTGA