FABRICATION AND CHARACTERIZATION OF PVA/STARCH FIBRE USING ELECTROSPINNING TECHNIQUE

NURUL FARHANA BINTI AHMAD

UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG

DECLARATION OF THESIS AND COPYRIGHT

Author's full name : Nurul Farhana Binti Ahmad

Date of birth : 25 January 1994

Title : Fabrication and Characterization of PVA/starch using Electrospinning Technique

Academic Session : Semester II 2016/2017

I declare that this thesis is classified as:

☐ **CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)

☐ **RESTRICTED** (Contains restricted information as specified by the organization where research was done)

■ **OPEN ACCESS** I agree that my thesis to be published as online open access (Full text)

I acknowledge that Universiti Malaysia Pahang reserve the right as follows:

1. The Thesis is the Property of Universiti Malaysia Pahang
2. The Library of Universiti Malaysia Pahang has the right to make copies for the purpose of research only.
3. The Library has the right to make copies of the thesis for academic exchange.

Certified By:

(Student's Signature)

Nurul Farhana Binti Ahmad
940125-06-5386
Date:

(Supervisor's Signature)

Dr. Farah Hanani bt Zulkifli

Date:

SUPERVISORS' DECLARATION

I hereby declare that I have checked the thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Hons) Material Technology.

Signature

Name of Supervisor : DR. FARAH HANANI ZULKIFLI

Position :

Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :

Name : NURUL FARHANA BINTI AHMAD

ID Number : SC13034

Date :

DEDICATION

Dedicated to the man that I respect my father Ahmad Bin Mohd Noor, my beloved mother, Bariah Binti Mat Ali, siblings Salwa, Busra, Nurul Fariha, Najiha and all my friends. You are my inspiration.

ACKNOWLEDGEMENTS

In the name of ALLAH, the most MERCIFUL and the most BENEVOLENT. All praise to ALLAH without whose help sustenance this study would never been complete. First of All, I would like to express my deepest gratitude to my supervisor, Dr Farah Hanani for her encouragement, guidance, critics and suggestion in supervise me throughout this year.

Furthermore, there is no other word to describe how grateful I am to the following individuals who help me in this study. Thanks to the lab assistant for helping me throughout the experiment. Not forgetting, my mother Bariah Bt Mat Ali and my siblings for the tremendous and endless support. Thank you for always stay by my side.

Last but not least, I would like to thank to my FYP II groupmate for helping me in this study and also to the other parties that involved directly or not in the process of finishing this study

ABSTRACT

In this research the polyvinyl alcohol (PVA) and starch are synthesized for the fabrication of fibre using electrospinning method. The fabrication of fibre for this research were prepared using four different ratio which were 100:0, 80:20, 60:40 and 50:50 of PVA/starch. The weight percent for the PVA and starch were 15wt% respectively. The obtained fibre were observed under the Scanning Electron Microscope (SEM) for the determination of the average diameter. The average diameter obtained for the four samples are 290.18 ± 26.24, 202.19 ± 37.75, 142.43 ± 25.96, 64.80 ± 8.26 respectively. For the TGA analysis, the first region of degradation is due to the loss of water content in the sample while the second and the third region is the decomposition of the main chemical chain and the decomposition of the main ring. The bond that had been detected in the sample tested are the O-H stretching, the C-H bending of CH_2 and the C-O-C bond. The viscosity obtained from the conducted test were 3337 cP, 3959 cP, 1284 cP and 82 cP for respectively. The conclusion that can be made is the 60:40 of the PVA:starch sample produced the best fiber based on the observation on the morphology, thermal properties and chemical properties.

ABSTRAK

Dalam kajian ini yang alkohol polyvinyl (PVA) dan kanji disintesis untuk fabrikasi gentian menggunakan kaedah electrospinning. Pembuatan serat untuk kajian ini telah disediakan dengan menggunakan empat nisbah yang berbeza iaitu 100: 0, 80:20, 60:40 dan 50:50 PVA / kanji. Berat peratus bagi PVA dan kanji masing-masing 15wt%. Serat diperolehi diperhatikan di bawah Mikroskop Imbasan Elektron (SEM) untuk menentukan diameter purata. Diameter purata diperolehi bagi empat sampel masing-masing 290.18 ± 26.24, 202.19 ± 37.75, 142.43 ± 25.96, 64.80 ± 8.26. Untuk analisis TGA, rantau pertama kemerosotan adalah disebabkan oleh kehilangan kandungan air dalam sampel manakala kedua dan kawasan yang ketiga ialah penguraian rantaian kimia utama dan penguraian cincin utama. Ikatan yang telah dikesan dalam sampel yang diuji adalah O-H regangan, C-H lenturan CH2 dan ikatan C-O-C. Kelikatan yang diperolehi daripada ujian yang dijalankan adalah 3337 cP, 3959 cP, 1284 cP dan 82 cP untuk masing-masing. Kesimpulan yang boleh dibuat ialah 60:40 daripada PVA: sampel kanji dihasilkan serat yang terbaik berdasarkan pemerhatian pada morfologi, sifat haba dan kimia.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

ml	-	mililitre
%	-	percent
µ	-	micron (10-6)
oC	-	degree celcius
mg	-	milligrams
wt%	-	weight percentage
cm-1	-	centimeters

LIST OF ABBREVIATIONS

PVA	-	Polyvinyl alcohol
ES	-	Electrospinning
ATR-FTIR	-	Attenuated total reflectance fourier transform infrared spectroscopy
TGA	-	Thermogravimetric analysis
SEM	-	Scanning electron microscope

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, a lot of industrial company use toxic materials for their production. The toxic materials that they use are non-biodegradable and harmful to the human kind. The environment effected by the non-degradable materials can cause pollution to the earth. A non-degradable material is a materials or waste from the industrial company that cannot be broken down into nonpoisonous or harmless substance. The example of non-degradable materials are polyethene bags, plastic bags, synthetic fibers, and many more. These materials are cost consuming however it still important for industries because of the needs of the production. The industries demand on non-toxic materials has increase since the world finally realize the important of it in order to avoid the global warming, the melt of the south and north poles, the draught and other environmental problems. The important properties for the non-toxic materials also include the cost effective for the production of product so that the cost can still under control. However, the suitable materials which are non-toxic still hard to be found because it is still new technology and still being develop by the researcher and other scientist. The new creation of non-toxic materials will help the industries to create product which is much more environmental friendly and biodegradable(Sadhu et al. 2014). Therefore, non-toxic materials such as bio-composite polymer becomes very important for various application industries if they want to reduce the usage of the toxic materials.

In this study, we will fabricated starch/PVA nanofibers by using electrospinning method. Starch is a carbohydrates that have a huge number of glucose. The glucose are bind together by glycosidic bonds. The polysaccharides basically being produced by almost all green plants and it is use as the energy storage. The carbohydrates that usually consume by the human can be found in potatoes, rice, wheat, corn and cassava. The second materials that will be used in this study is polyvinyl alcohol (PVA). The PVA are non-toxic, because it can be biodegrade slowly. In this research, we will use deionized water as the solvent which is not cause any harm to the environment and the human.

1.1 Statement of the problem

The demand of the non-toxic products are increase nowadays and the researchers need to find a way to develop ecofriendly and naturally degradable materials to be used in various field in industries (i.e., tissue engineering, water filter and sensor). It is crucial to provides materials that is safe to the human kind that will not cause any defect to the DNA and their health. Thus, it is important to done continuous research to develop the new biomaterials which is not only cost-effective but safe and applicable to the industries around the world.

1.2 Objectives of the study

The objectives of the study are to:

i) To develop starch and starch-loaded PVA fiber using the electrospinning method.
ii) To study the morphology, chemical and thermal properties of the composite materials

1.3 Scope of the study

To achieve the first objective, the scope of study are

i) To optimize the parameter of the of the electrospinning technique and to analyze the samples using different ratio of starch-to-PVA.

For the second objectives the scope of study are

i) To observe the morphology of starch/PVA fibers using scanning electron microscope (SEM).

ii) To study the chemical properties of the starch and PVA fibers using the ATR-FTIR

iii) The thermal properties will be investigate using Thermo Gravimetric analysis (TGA).

iv) The viscosity of the starch-to-PVA using different ratio will be determine using the viscometer.

CHAPTER 2

LITERATURE REVIEW

2.1 BIOPOLYMER MATERIALS

Biopolymer is a materials that is biodegradable and safe to nature. The structure of the biopolymer are long because it is consist of repeatable units monomers. Biopolymer such as starch is commonly used in various industries due to low cost and easily obtained by natural resource (Wiacek 2015). Starch is commonly being modified with other materials such as starch to enhance the properties for various application.

2.1.1 Starch

Starch has a chemical formula of $(C_6H_{10}O_5)_n$ and have variables molar mass. It has physical appearance as white powder or granule (Huang et al. 1994). Starch basically has no taste and odor. The density if starch is $1.5\ g/cm^3$.

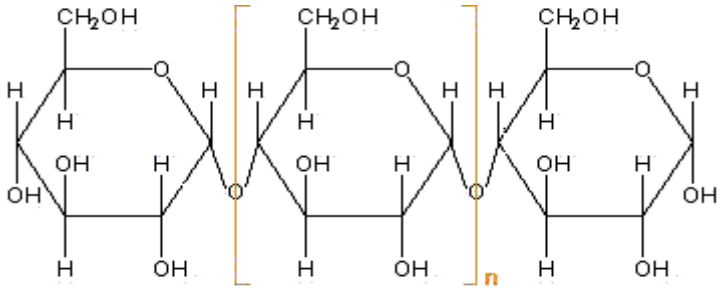


Figure 2.1.1 **:** The structure of starch made of many units of monomers

Source: Reproduced from (Wikipedia 2016)

Starch consist of two main component which are amylose and amylopectin. Starch that contain high number of amylose are strong and able to produce strong film which make it suitable in plastic production (Jane 1995). It is soluble in water. Starch can be obtain from natural resource such as potatoes, rice, wheat and cassava.

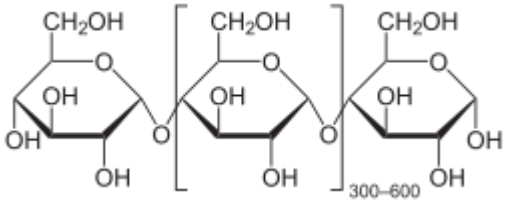


Figure 2.1.1 **:** The structure of amylose
Source: Reproduced from (Wikipedia 2016)

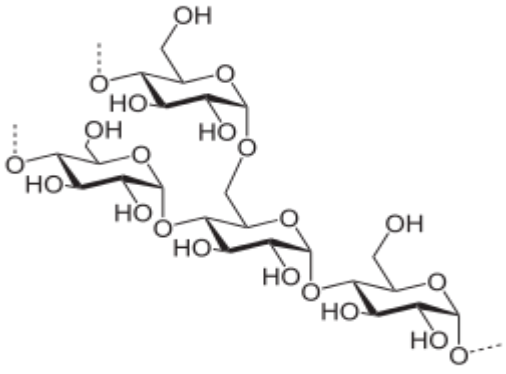


Figure 2.1.1 **:** The structure of Amylopectin
Source: Reproduced from (Wikipedia 2016)

2.1.2 Polyvinyl Alcohol (PVA)

Polyvinyl alcohol is a synthetic polymer and one of the largest produced polymer throughout the years because of its outstanding chemical and physical properties (Guirguis

& Moselhey 2012). PVA is one of the most common polymer that being blended or mixed with other natural polymer because it is can be easily altered or manipulated by the amount of water as the solvent (Journal 2011). There is a lot of application that use PVA as the main materials such as in biomedical field and pharmaceutical field (Hassan & Peppas 2000). It has chemical formula of $(C_2H_4O)_n$ and has physical appearance of pure PVA are white granule-like texture. The density of PVA is 1.31 g/cm^3 which is denser that water. The melting and boiling point of the PVA are 200 C° and 228 C°. Figure 2.1.2 show the structure of PVA.

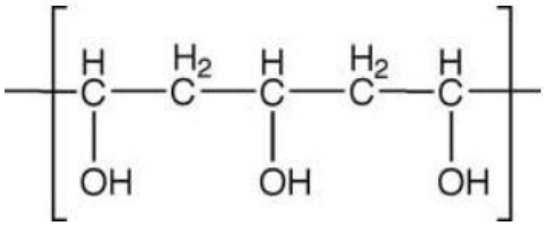


Figure 2.1.2 **:** The structure of PVA
Source: Reproduced from (Wikipedia 2016)

2.2 ELECTROSPINNING TECHNIQUE

Electrospinning is a scientific technique that have the capability to produce a tiny diameter of fiber up to micro and nanometer. The electrospinning consist of a spinneret (hypodermic needle) that is connected to the high voltage direct current. The polymer will be electrospun from the needle at constant rate and high speed to produce very high surface to volume ratio, and a relatively defect free structure at the molecular level nanofibers(Agarwal, Greiner, & Wendorff, 2013).

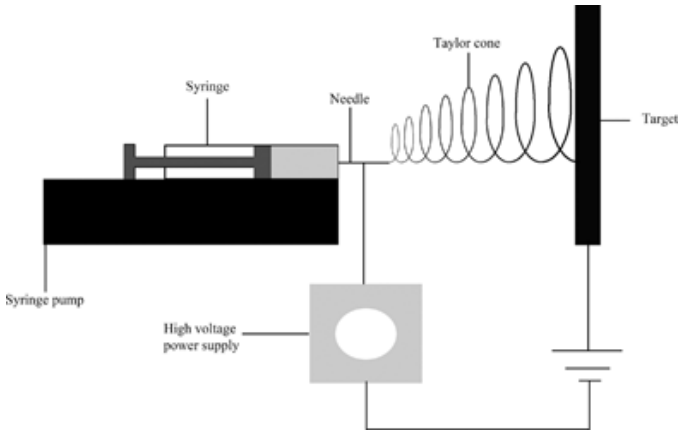


Figure 2.2.1 **:** The setup of electrospinning technique
Source: Reproduced from (Wikipedia 2016)

2.3 CHARACTERIZATION ANALYSIS

2.3.1 Scanning Electron Microscope (SEM)

SEM is a tool to study the morphology of a materials which is in this case the nanofibers. The SEM working principle contain electron gun, condenser lens, scanning coil, objective lens and sample holder (JEOL Ltd. n.d.).

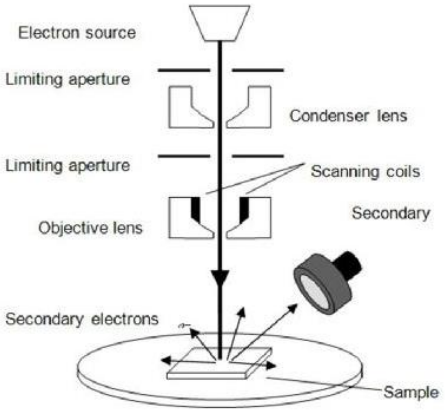


Figure 2.3.1 **:** The schematic diagram of SEM
Source: Reproduced from (Wikipedia 2016)

2.3.2 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FTIR)

FTIR is an analysis use to study the chemical properties of a materials. Attenuated Total Reflectance is a one of the most famous sampling that we use for FTIR because it make the analysis process to be done in a short period of time since the samples require less or no preparation at all unlike the regular FTIR analysis that need the sample to be pressed into pellets form (Pike Technologies 2014).

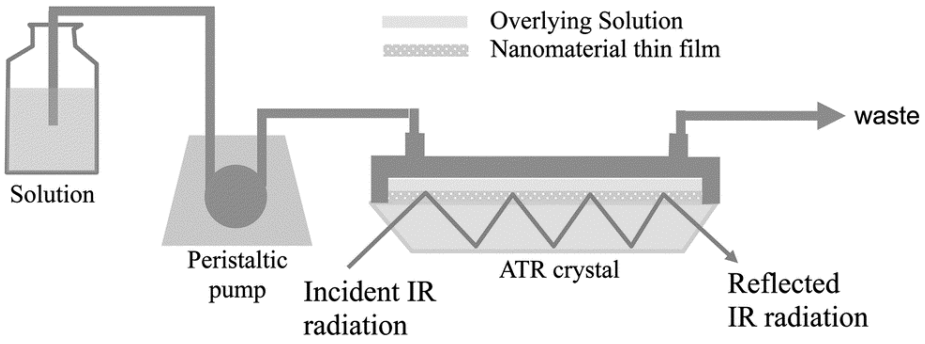


Figure 2.3.2 **:** The schematic diagram of ATR-FTIR
Source: Reproduced from (Wikipedia 2016)

2.3.3 Thermogravimetry analysis (TGA)

Thermogravimetry analysis is an analysis use to determine the thermal properties of a solution (Idris et al. 2010). In this research the thermal properties of starch and starch-to-PVA will be observe and determine using TGA. Figure 2.2.3 show the instrument of TGA.

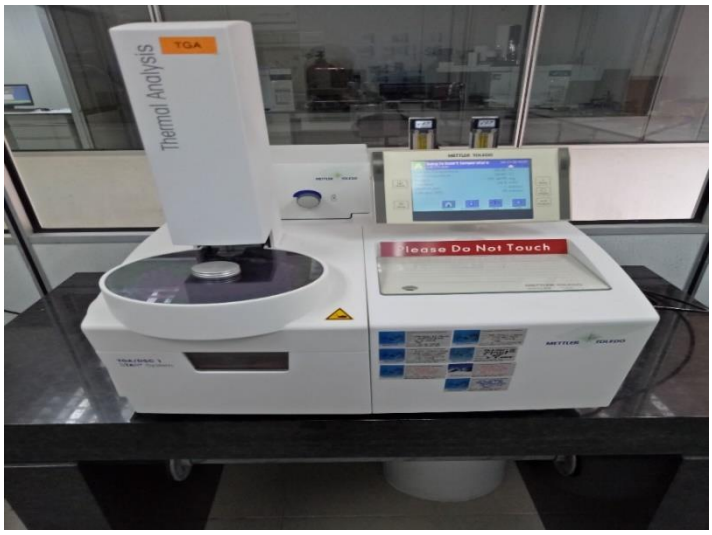


Figure 2.3.3 : The instrument of TGA

2.3.4 Viscometer

Viscometer is a tool used to determine the viscosity of solution. The viscosity of the solution can be determine by placing the solution in a beaker and insert the spindle until its mark is completely immerse in the solution. Then, the rotational speed can be choose by the user and the time limit for the rotation is assigned before the operation can be start. Figure 2.3.4 show the viscometer instrument.

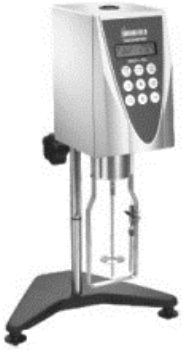


Figure 2.3.4 : The Viscometer BROOKFIELD,USA (LVDV 1)

CHAPTER 3

RESEARCH METHODOLOGY

Poly (vinyl alcohol) with molecular weight 95000 were purchased from ACROS Organics, New Jersy, USA .In this research the method that were used was by using electrospinning technique to form the fibers. The research started with the synthesis of the starch and PVA polymer solution.

3.1 SYNTHESIS OF STARCH AND PVA SOLUTION

Firstly, the wheat starch was being dilute with the Millipore water in a 500 ml Schott botlle .The weight percent for the wheat starch to Millipore water were 15wt% Then, by using the magnetic stirrer, the solution is being stirred continuously for 24 hours at room temperature until all the starch dissolved in the solvent.

For the PVA, the 75g of PVA was added to 500 ml Millipore water for the 15wt% of the solution. The solution were heat to $80°C$ to ensure the PVA were completely dissolve in the solvent with continuous stir for 7 days at room temperature.

The sample preparation for the testing will be prepared by adding the PVA and starch solution into one beaker. The ratio of the mixture are 100:0, 50:50, 60:40 and 80:20 of PVA/starch.

3.2 THE FABRICATION OF FIBER

The mixture of PVA/starch was filled in a syringe fitted with a blunt steel needle of 0.8 mm inner diameter and flow rate of 0.05 ml/h. The applied voltage used 20 kV. The electrospun nanofibers were collected using a rotating drum collector wrapped with aluminum foil at the distance of 6 cm from tip-to-collector. The collected nanofibers were stored in desiccators for further use. The same parameter was use for all the sample.

Figure 3.2: The fabrication of PVA/starch using electrospinning technique**.**

3.3 THE CHARACTERIZATION ANALYSIS

3.3.1 Scanning Electron Microscope

In this research SEM- CARL ZEISS Evo50 brand is used for imaging of sample surfaces at high magnification and resolution. It provided the morphology of the samples

Figure 3.3.1 : Scanning Electron Microscope CARL ZEISS Evo50

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

The ATR-FTIR is used to characterized the chemical compound exist in a sample. It show the chemical bonding that occur in the tested sample. The scanned region for the ATR-FTIR is between 700 cm^{-1} to 4000 cm^{-1}. The infrared spectroscopy that obtained were recorded in the complete software system in computer.

Figure 3.3.2: ATR-FTIR , Pelkin Elmer Spectrum 100

3.3.4 Thermogravimetric analyzer (TGA)

In this research the thermal properties of the sample was carried out using the Mettler Toledo-TGA/DSC1. The equipment has the microbalance and thermocouple sensor to measure heat flow as well as weight change as function of temperature. The equipment also has broad temperature measurement up to 1000 ^{0}C. It come with a build in mass controller that contain hydrogen gas to control the atmospheric around the sample.

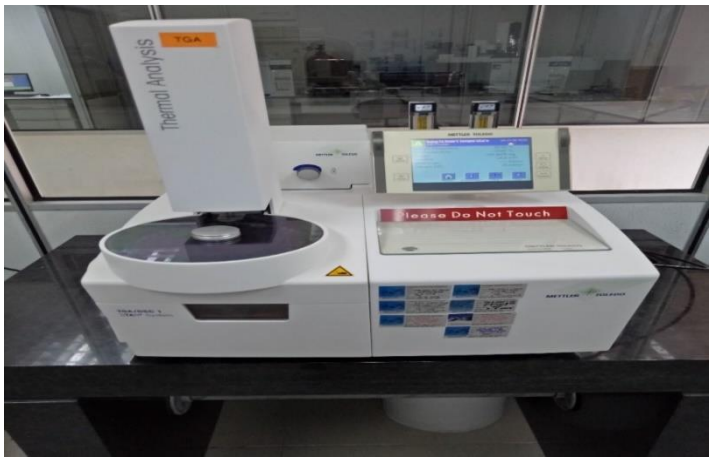


Figure 3.3.4: Mettler Toledo-TGA

3.3.5 Viscosity test

Viscometer is a tool used to determine the viscosity of solution. The viscosity of the solution can be determine by placing the solution in a beaker and insert the spindle until its mark is completely immerse in the solution. Then, the rotational speed can be choose by the user and the time limit for the rotation is assigned before the operation can be start. Figure 2.3.4 show the viscometer instrument.

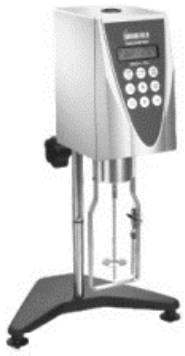


Figure 3.3.5 : The Viscometer BROOKFIELD,USA (LVDV 1)

CHAPTER 4

RESULT AND DISCUSSION

INTRODUCTION

The main objective of this part is to develop a fiber made of starch and PVA using the electrospinning method using different ratio. The materials which are wheat starch and fiber are solute using the milipore water as the solvent. The morphology of the obtained fiber were characterized using SEM,ATR-FTIR, TGA and viscosity and conductivity test.

MORPHOLOGY OF STARCH/PVA

4.1 Scanning Electron Microscope

The average diameter for the 100% PVA are the largest compare to the 80:20, 60:40, and 50:50 PVA/Starch which is 290.18 nm. The smallest fibers obtained from the sample is from the 50:50 PVA/Starch with the average diameter of 64.8 nm. As for the 80:20 and 60:40 of PVA/Starch the average diameter are 202.19 nm and 142.43 nm respectively. Table 4.1 show the electrospinning parameters for PVA/Starch fiber and their corresponding average fiber diameter

Table 4.1
The electrospinning parameters for the samples

Sample Code	Electrospinning parameters.			
	Tips-to-collector distance (cm)	Flow rate (ml/h)	Applied voltage (kV)	Average fiber diameter (nm)
100:0	6	0.05	20	290.18 ± 26.24
80:20	6	0.05	20	202.19 ± 37.75
60:40	6	0.05	20	142.43 ± 25.96
50:50	6	0.05	20	64.80 ± 8.26

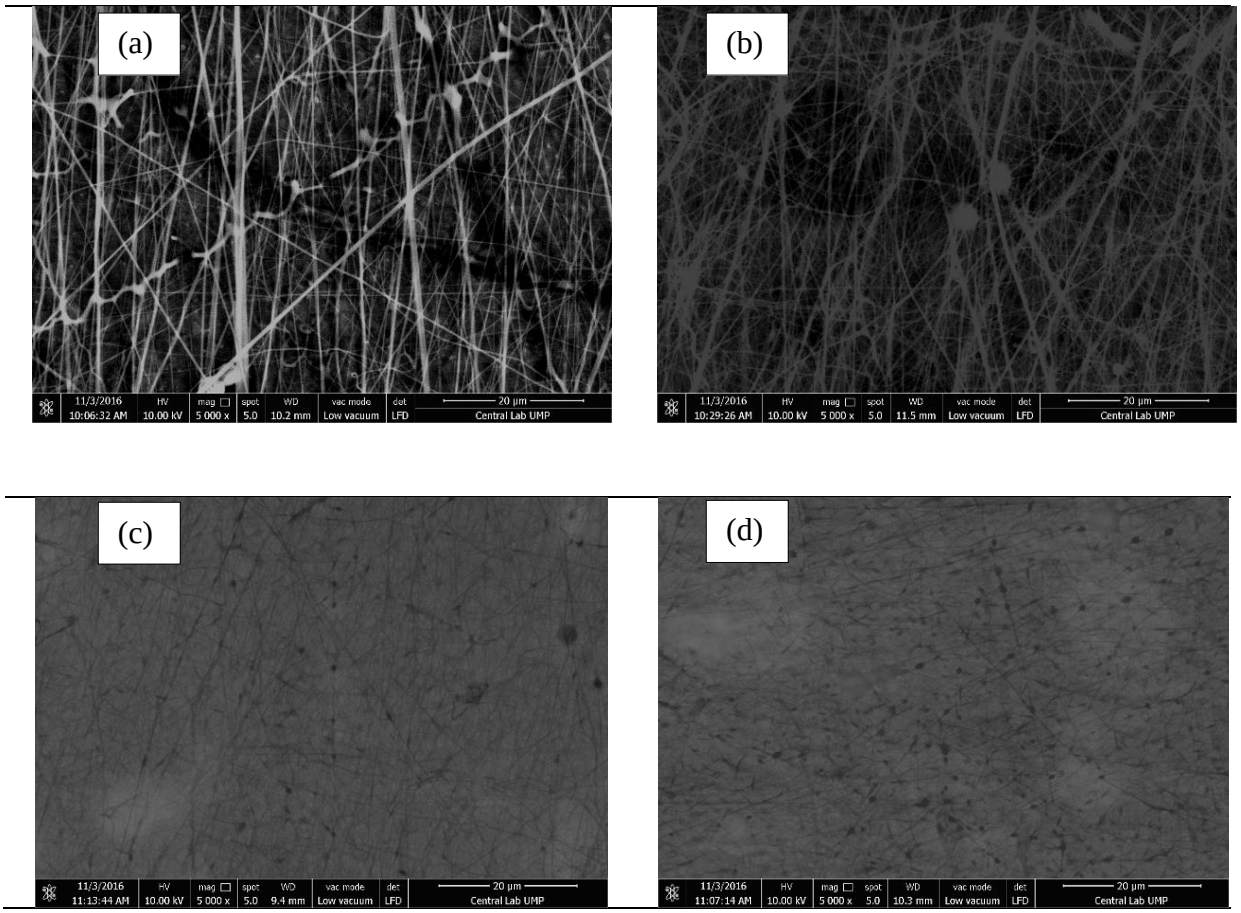
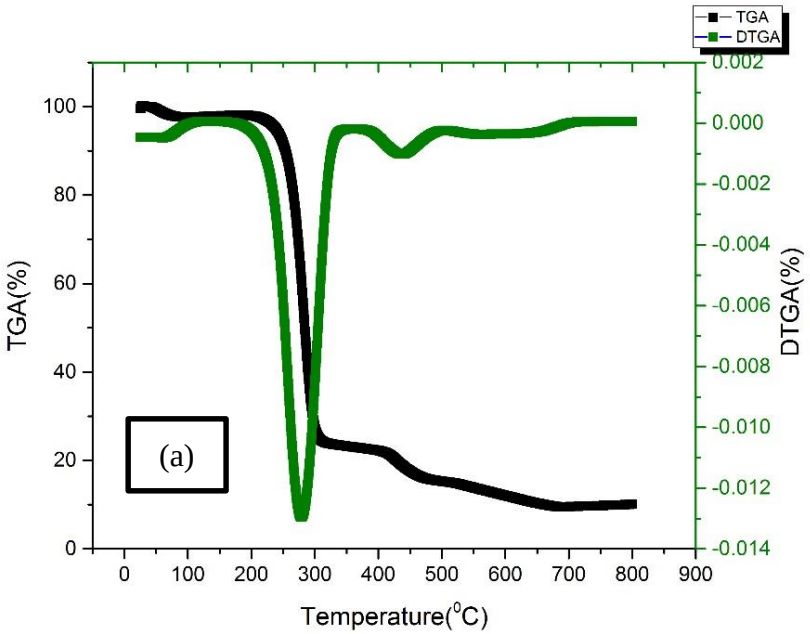
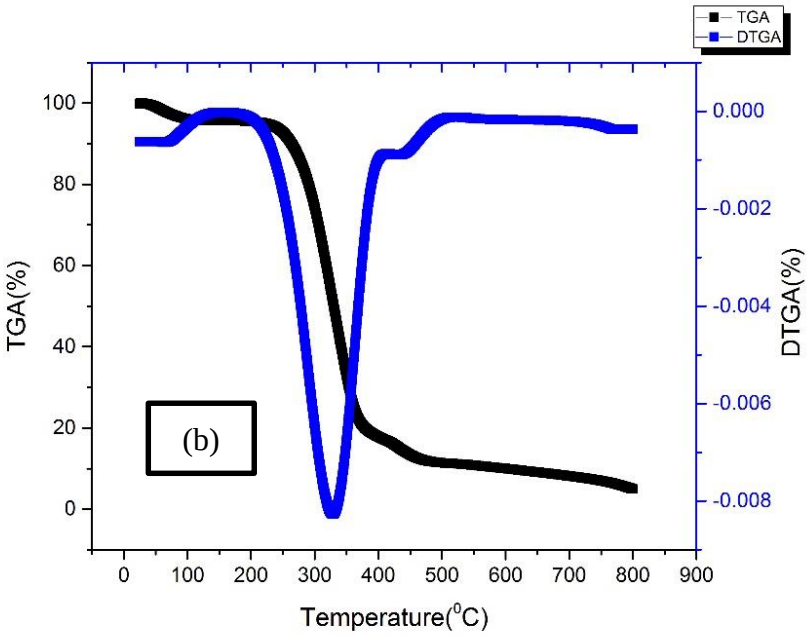


Figure 4.1: SEM images and diameter distribution of electrospun PVA/Starch nanofibers: (a) 100:0, (b) 80:20, (c) 60:40, (d) 50:50

4.2 Thermogravimeter analysis

TGA analysis was conducted to observe the weight loss behavior of the PVA/starch fiber. The thermal degradation of four samples are shown in the figure.





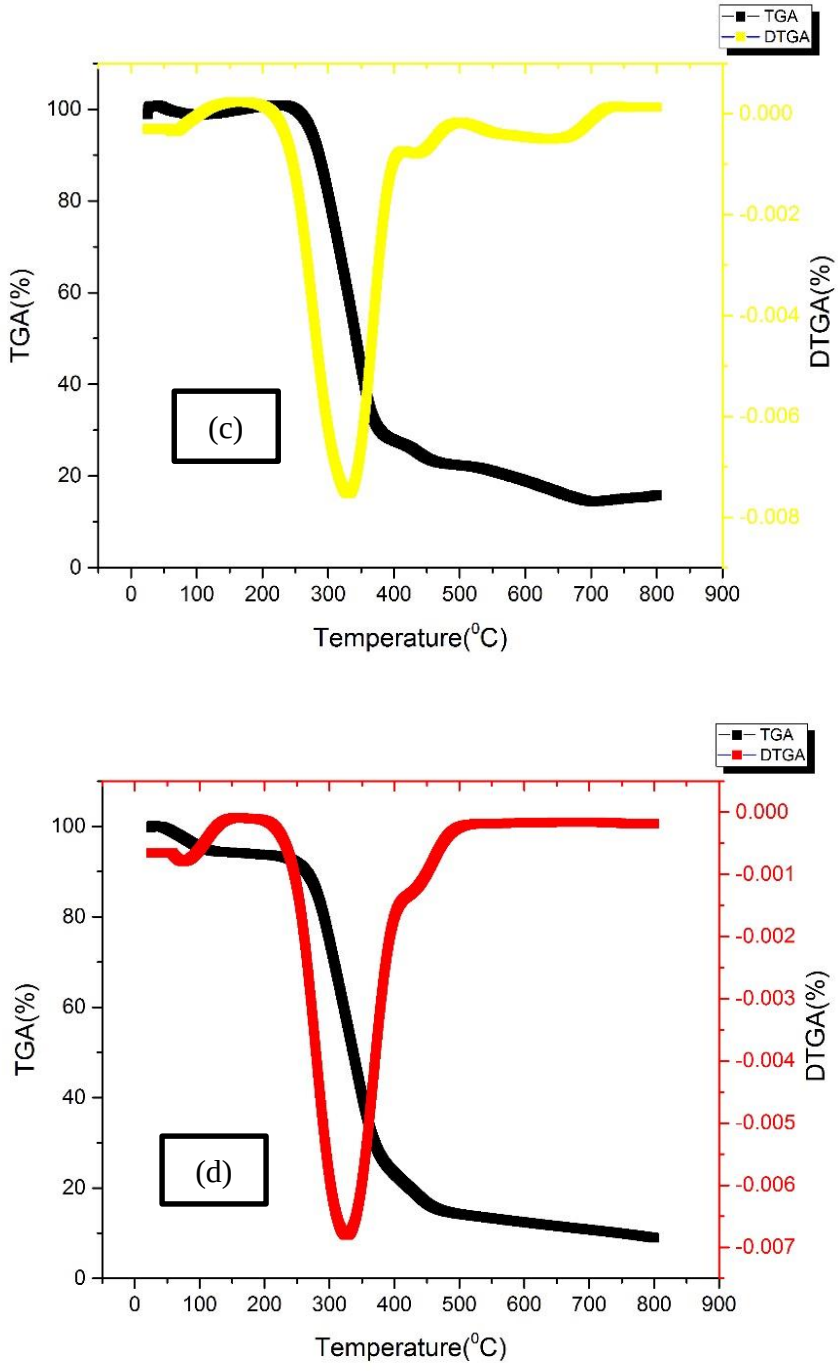


Figure 4.2 : (a) 100.0, (b) 80:20 ,(c) 6040 and (d) 50:50 of PVA:starch

Table 4.2
Thermal data for fiber samples

Properties	**100:0**	**80:20**	**60:40**	**50:50**
Quantity(mg)	1.5166	2.8678	0.5880	3.3080
Heating rate(°C/min)	10	10	10	10
Heating degree (°C)	800	800	800	800

Table 4.2
TGA and DTGA data

Sample	**Region of decomposition**	**Temperature (^{0}C)**			**Weight loss (%)**	
		T_{start}	**T_{end}**	**T_{peak}**	**Partial**	**Total**
100:0	1st	22.09	131.29	72.08	3.88	96.4
	2nd	131.29	359.52	278.57	84.74	
	3rd	359.52	524.68	433.55	7.78	
80:20	1st	17.09	108.22	65.37	4.44	98.74
	2nd	108.22	387.01	315.10	88.23	
	3rd	387.01	478.52	420.09	6.07	
60:40	1st	20.56	156.49	91.13	3.44	92.1
	2nd	156.49	256.06	275.11	82.23	
	3rd	256.06	504.11	428.35	6.43	
50:50	1st	22.29	144.64	68.61	6.63	97.57
	2nd	142.64	336.06	288.96	87.77	
	3rd	356.06	500.64	419.70	3.17	

The table show the percentage of weight loss TGA% with the derivative mass loss DTGA% for three major region. The first weight loss are usually due to the loss of water content in the sample (Yai 2013). The water loss can be seen in the first region that has low temperature. For the second region show the higher temperature range 131.29 °C to 524.68

^{o}C.The broad range weight loss indicate major degradation of chemical process (Guirguis & Moselhey 2012). The second region shows the decomposition of polymeric and the chain of PVA and the dehydration of the polysaccharides rings in the starch (Yai 2013). The third weight loss of the sample is due to the degradation process to decompose the main ring and chain.

4.3 Attenuated total reflection-Fourier transform reflection (ATR-FTIR)

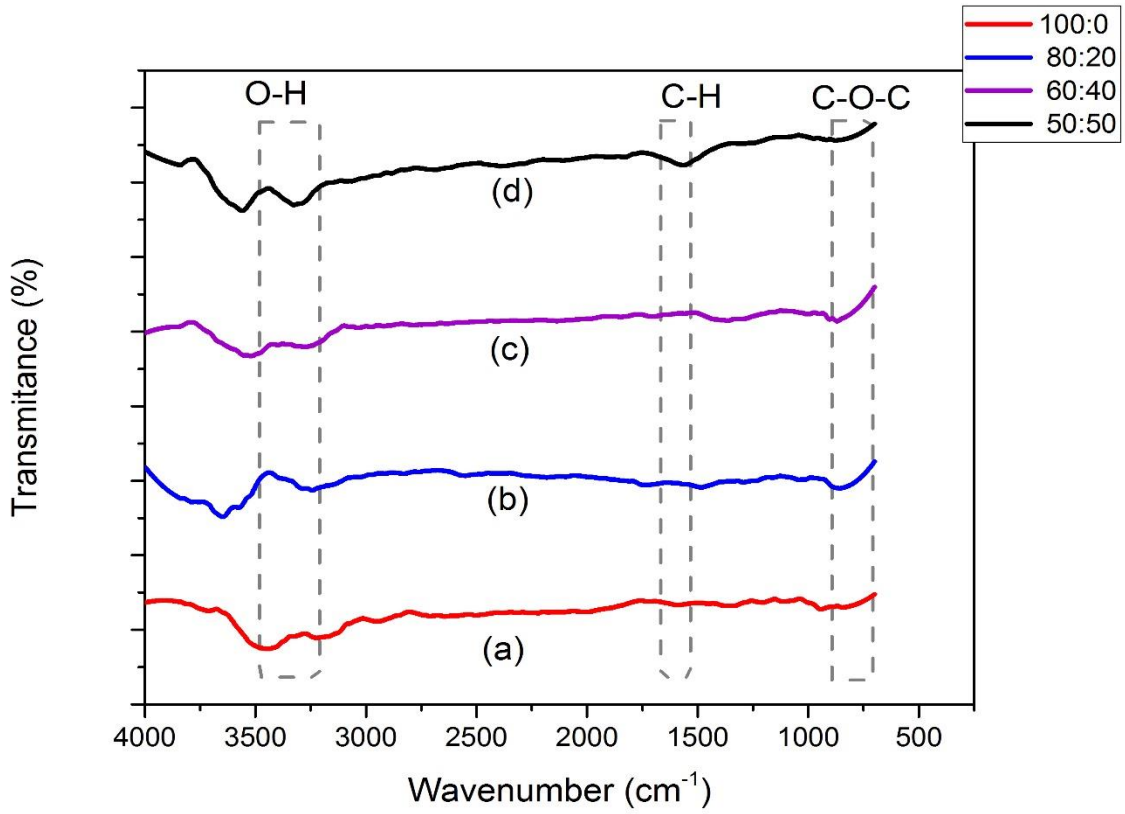


Figure 4.3 **:** ATR-FTIR spectroscopy of a) 100.0, (b) 80:20 ,(c) 6040 and (d) 50:50 of PVA:starch

ATR-FTIR

The chemical structure when the PVA solution that was mixed with starch is change slightly. It has the slope at the range of 775 cm^{-1} where the stretching vibration C-O of C-O-C occurred. At the range of 3200 to 3500 is where the O-H bonding occurred. At the 1455 cm^{-1} the C-H bending of CH_2 appear. The O-H bending and C-H bending of CH_2 that occur in the spectra show that the PVA and the starch are completely blend (Râpă et al. 2014).

4.4 Viscosity test

Viscosity is one of the parameter that affect the electrospinning of the fibers. The ratio for the sample tested were 100:0, 80:20, 60:40, 50:50 of PVA : starch. From the data obtained , it shows that the 80:20 ratio had the highest viscosity which was 3959 cP. The 50:50 ratio had the lowest viscosity which was 82 cP. The viscosity for 100:0 and 60:40 ratio samples were 3337 cP and 1284 cP respectively. The viscosity of the sample decrease as the ratio of the starch increase. Table 4.1 show the data obtained for the viscosity test.

Table 4.4
The Viscosity data of 100.0, 80:20 , 6040 and 50:50 of PVA:starch

Sample	Speed(rpm)	Result(cP)	Test Method
100:0	8.0	3337	In-House Method based on Brookfield LV-DVII
80:20	1.4	3959	In-House Method based on Brookfield LV-DVII
60:40	22.0	1284	In-House Method based on Brookfield LV-DVII
50:50	6.0	82	In-House Method based on Brookfield LV-DVII

CHAPTER 5

RECOMMENDATION AND CONCLUSION

1.1 Introduction

This chapter highlighted the recommendation and conclusion furthered with discussion.

1.2 CONCLUSION

In this study, the sample with ratio of 60:40 PVA/starch with 15wt% and 15wt% respectively are the easiest for the fabrication of the fiber. The sample produced the best fiber based on the observation on the morphology, thermal properties and chemical properties.

1.3 RECOMMENDATION FOR FUTURE RESEARCH

Recommendations that I would like to suggest to improve the result of the research is to ensure that the solution is handle properly to avoid contamination that may affect the result. When the solution are mixed, make sure the sample is on continuous stirring to avoid the PVA and starch solution from separated. When the heat is applied during the preparation of the stock solution for PVA, make sure that the heat is not over $80°C$ so that it will not affect the properties of the solution. When the experiment is conduct, wear the proper Personal Protective Equipment (PPE) for the safety reasons.

In this study the further suggestion that can be made is to test the fiber sample using other characterization such as tensile test and strength. The other suggestion that can be made is

to use other method other than electrospinning technique for example freeze- dry technique and casting.

REFERENCES

Guirguis, O.W. & Moselhey, M.T.H., 2012. Thermal and structural studies of poly (vinyl alcohol) and hydroxypropyl cellulose blends. *Natural Science*, 4(1), pp.57–67.

Hassan, C.M. & Peppas, N. a, 2000. Structure and Applications of Poly (vinyl alcohol) Hydrogels Produced by Conventional Crosslinking or by Freezing / Thawing Methods. *Adv. Polym. Sci.*, 153, pp.37–65.

Huang, R. et al., 1994. Phase transitions of rice starch and flour gels. *Cereal Chemistry*, 71, pp.202–207.

Idris, S.S. et al., 2010. Investigation on thermochemical behaviour of low rank Malaysian coal, oil palm biomass and their blends during pyrolysis via thermogravimetric analysis (TGA). *Bioresource Technology*, 101(12), pp.4584–4592. Available at: http://dx.doi.org/10.1016/j.biortech.2010.01.059.

Jane, J., 1995. Starch Properties, Modifications, and Applications. *Journal of Macromolecular Science, Part A*, 32(4), pp.751–757. Available at: http://www.tandfonline.com/doi/abs/10.1080/10601329508010286.

JEOL Ltd., Scanning Electron Microscope A To Z. , pp.1–32.

Journal, M.P., 2011. Thermal Properties of Polyvinyl Alcohol (PVOH)/Corn Starch Blend Film NADRAS OTHMAN*, NUR AZLEEN AZAHARI, HANAFI ISMAIL . *Polymer Journal*, 6(6), pp.147–154.

Pike Technologies, 2014. APPLICATION NOTE ATR – Theory and Applications. *Pike Technologies*, pp.1–3.

Râpă, M. et al., 2014. Journal of Environmental Research and Protection Polyvinyl alcohol and starch blends : properties and biodegradation behavior. , 11(1), pp.34–42.

Sadhu, S.D., Soni, A. & Varmani, S.G., 2014. Preparation of Starch-Poly Vinyl Alcohol (PVA) Blend Using Potato and Study of Its Mechanical Properties Meenakshi Garg. , 3(3), pp.33–37.

Wiacek, A.E., 2015. Effect of surface modification on starch biopolymer wettability. *Food Hydrocolloids*, 48, pp.228–237.

Yai, H., 2013. Mechanical , thermal and structural properties of rice starch films reinforced with rice starch nanocrystals. , 20(1), pp.439–449.