การผลิตเส้นใยคาร์บอนจากลิกนินของเปลือกไม้ยูคาลิปตัสโดยใช้การปั่นเส้นใยด้วยไฟฟ้าสถิตย์

นายมานิต พูลสวัสดิ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2556

PRODUCTION OF CARBON FIBERS FROM EUCALYPTUS BARK LIGNIN BY ELECTROSPINNING

Mr. Manit Pulsawad

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2013

Thesis Title	PRODUCTION OF CARBON FIBERS FROM EUCALYPTUS BARK LIGNIN BY ELECTROSPINNING
By	Mr.Manit Pulsawad
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Varong Pavarajarn, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering

(Professor Bundhit Eua-Arporn, Ph.D.)

THESIS COMMITTEE

....Chairman

(Jirdsak Tscheikuna, Ph.D.)

....Thesis Advisor

(Assistant Professor Varong Pavarajarn, Ph.D.)

....Examiner

(Assistant Professor Apinan Soottitantawat, Ph.D.)

....External Examiner

(Bussarakum Charnhattakorn, D.Eng.)

มานิต พูลสวัสดิ์ : การผลิตเส้นใยคาร์บอนจากลิกนินของเปลือกไม้ยูคาลิปตัสโดยใช้การปั่นเส้นใยด้วยไฟฟ้าสถิตย์ (PRODUCTION OF CARBON FIBERS FROM EUCALYPTUS BARK LIGNIN BY ELECTROSPINNING) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.วรงค์ ปวราจารย์, 66 หน้า.

กระบวนการอิเลกโตรสปินนิ่งหรือการปั่นเส้นใยด้วยไฟฟ้าสถิตย์ถูกใช้เพื่อผลิตเส้นใยคาร์บอนไฟเบอร์จากลิกนินชนิดต่างๆได้แก่ ลิกนินจากการขายเชิงพานิชย์โดยกระบวนการคราฟท์, ลิกนินจากไม้เนื้อแข็งและ ลิกนินจากเปลือกไม้ของไม้เนื้อแข็ง ไม้และเปลือกไม้ ของไม้เนื้อแข็งถูกสกัดเพื่อให้ได้ลิกนินด้วยกระบวนการโซดาโดยใช้โซเดียมไฮดรอกไซด์ ลิกนินทั้งสามชนิดถูกนำมาวิเคราะห์หมู่ฟังก์ชั่น ความหนืด และคุณสมบัติด้านความร้อน โดยผลพบว่าลิกนินที่ได้มาจากการขายเชิงพานิชย์น่าจะเป็นลิกนินที่ผลิตมาจากไม้เนื้ออ่อน ซึ่งมีน้ำหนักโมเลกุลสูงสุด สำหรับลิกนินจากไม้ของไม้เนื้อแข็งมีน้ำหนักโมเลกุลรองลงมา และลิกนินจากเปลิกไม้มีน้ำหนักโมเลกุลต่ำที่สุด

ลิกนินถูกละลายด้วยตัวทำละลายไดเมททิลฟอร์มัลเอไมด์ (ดีเอ็มเอฟ) เพื่อให้ได้ความเข้มข้นต่างๆกัน พอลีเอททิลลีนออกไซด์ (พีอีโอ) ถูกเติมเข้าไปเพื่อช่วยในการผลิตเส้นใย เส้นใยที่ได้จากการปั่นเส้นใยด้วยไฟฟ้าสถิตย์ถูกวิเคราะห์คุณสมบัติด้านการภายโดยใช้กล้องจุลทรรศน์อิเล็กตรอน ผลปรากฏว่าเส้นใยที่ผลิตจาก ลิกนินของไม้เนื้ออ่อนและลิกนินของไม้ของไม้เนื้อแข็งมีรูปร่างทางการภาพที่ดี แต่ลิกนินจากเปลือกไม้นั้นมีขนาดของเส้นใยที่แตกต่างกันมากและการจัดเรียงของเส้นใยไม่เป็นระเบียบ นอกจากนี้พบว่า การเพิ่มความต่างศักย์และระยะระหว่างปลายเข็มถึงแผ่นรองรับส่งผลต่อขนาดเส้นใยและการผลิต เส้นในที่ได้ถูกนำไปเผาเพื่อให้ได้เป็นคาร์บอนไฟเบอร์ และพบว่ารูปร่างทางกายภาพของเส้นใยคาร์บอนไฟเบอร์มีลักษณะที่ดี มีการละลายติดกันของเส้นใยที่มีขนาดเล็กบ้าง

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต
สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก
ปีการศึกษา 2556

5271559821 : MAJOR CHEMICAL ENGINEERING
KEYWORDS : BARK LIGNIN / CARBON FIBER/ ELECTROSPINNING

MANIT PULSAWAD : PRODUCTION OF CARBON FIBERS FROM EUCALYPTUS BARK LIGNIN BY ELECTROSPINNING. ADVISOR : ASST. PROF. VARONG PAVARAJARN, Ph.D., 66 pp.

Electrospinning process was used to prepare carbon fibers from three types of lignin including Commercial Kraft Lignin (CKL), Wood Soda Lignin (WSL) and Bark Soda Lignin (BSL). Wood and Bark lignin was extracted from Eucalyptus wood by soda pulping process. The lignin was characterized by FT-IR spectrometer, viscometer and thermal gravimetric analysis. The lignin was dissolved in DMF at various concentrations and PEO were used as polymer blender. The solution was electrospun using various conditions. Lignin fibers were characterized by scan electron microscope to investigate their morphology. Uniform fibers could be formed from CKL and WSL precursor, while the fibers from BSL lignin resulted in non-uniform short fibers. The average diameter of the fibers was affected by both applied voltage and the distance between tip and collector. Carbon fibers could be formed by stabilizing and carbonizing the lignin fibers.

Department : Chemical Engineering Student's Signature
Field of Study : Chemical Engineering Advisor's Signature
Academic Year : 2013

ACKNOWLEDGEMENTS

The author would like to acknowledge to his advisor, Assistant Professor Dr. Varong Pavarajarn, Department of Chemical Engineering, Chulalongkorn University for his high valuable advised, support and help. In addition I would like to thank you Dr.Jerdsak Tscheikuna as the chairman, Assistant Professor Dr. Apinan Soontitantawat, and Dr. Bussarakam Charnhattakorn, members of the thesis committee for their kind cooperation, comments and discussions.

Many thanks to all my friends in the Center of Excellent in Particle Technology for kindly help and suggestion.

CONTENTS

Page

ABSTRACT IN THAI iv

ABSTRACT IN ENGLISH v

ACKNOWLEDGEMENTS vi

CONTENTS vii

LIST OF TABLES ix

LIST OF FIGURES x

CHAPTER

I INTRODUCTION 1

II THEORY AND LITERATURE SURVEY 5

- 2.1 Lignin 5
  - 2.1.1 Structure of lignin 5
  - 2.1.2 Technical lignins 8
- 2.2 Alkaline processes and lignin precipitation 9
- 2.3 Physical properties of carbon fiber 10
- 2.4 Electrospinning 11

III EXPERIMENTAL 18

- 3.1 Materials 18
- 3.2 Pulping Apparatus 20
- 3.3 Electrospinning Apparatus 20
- 3.4 Experimental Procedure 21
  - 3.4.1 Material preparation 21
  - 3.4.2 Lignin extraction 22
  - 3.4.3 Lignin precipitation 22

3.4.4 Solution preparation 22

3.4.5 Electrospinning 23

3.4.6 Thermostabilization and Carbonization 23

3.5 Sample Charaterizations 23

3.5.1 Scanning Electron Microscope 23

3.5.2 Viscosity measurement 24

3.5.3 Fourier transform infared spectroscopy (FT-IR) 24

3.5.4 Thermal gravimetric analysis (TGA) 24

IV RESULTS AND DISCUSSION 25

4.1 Characterization of raw material 25

4.1.1 FT-IR spectra of lignin 25

4.1.2 Thermal behavior of Lignin 30

4.1.3 Viscosity of Lignin solution 32

4.2 Effect of solution parameter on electrospinning process 33

4.3 Effect of process condition on electrospinning process 36

4.3.1 Morphology of CKL fiber 36

4.3.2 Morphology of WSL fiber 38

4.3.3 Morphology of BSL fiber 40

4.3.4 Effect of voltage on diameter of fiber 42

4.3.5 Effect of the distance between tip and collector on diameter 44

4.3.6 Effect of increasing the viscosity 45

4.4 Morphology of carbon fiber 46

V CONCLUSION 48

REFERENCES 50

VITA 55

LIST OF TABLES

Page

2.1 Percentage of lignin in various biomass sources 6
2.2 Lignin compositions by sources 7
2.3 Chemical properties of the technical lignins 8
2.4 Solution to spinning problems 10
3.1 List of chemical agents used in the research 18
3.2 Chemical structure of compound used in this research 19
4.1 Summary of IR bands associated with different types of bonds 28
4.2 Viscosity of Lignin/DMF solution 32

LIST OF FIGURES

Page

2.1 Types of C9 units found in lignin 6

2.2 General structure of native lignin 7

2.3 Structure of graphitic crystals 11

2.4 Scheme for electrospinning equipment 12

3.1 Schematic of pulping setup 20

3.2 Schematic of electrospinning setup 21

4.1 FTIR spectrum of commercial kraft lignin (CKL) 26

4.2 FTIR spectrum of wood soda lignin (WSL) 26

4.3 FTIR spectrum of bark soda lignin (BSL) 27

4.4 Thermal behavior of CKL 30

4.5 Thermal behavior of WSL 31

4.6 Thermal behavior of BSL 31

4.7 SEM image of the droplet on the collector of 50%wt of WSL system 33

4.8 SEM images of CKL 45% solution electrospun at 15cm, 15kV (a) and 20 cm, 15 kV (b) 34

4.9 SEM image of CKL 40% solution electrospun at 20cm, 20kV 35

Page

4.10 SEM image of CKL 40% solution electrospun at 15cm 10kV (a), 15cm 15kV (b), 15cm 20kV (c), 20cm 10kV (d), 20cm 15kV (e), 20cm 20kV (f) 37

4.11 SEM image of WSL 40% solution electrospun at 20cm 10kV (a), 20cm 15kV (b), 20cm 20kV (c), 25cm 10kV (d), \ 25cm 15kV (e), 25cm 20kV (f) 39

4.12 SEM image of BSL 40% solution electrospun at 20cm 10kV (a), 20cm 15kV (b), 20cm 20kV (c), 25cm 10kV (d), 25cm 20kV (e) 41

4.13 Relation between applied voltage and average fiber diameter of CKL system 42

4.14 Relation between applied voltage and average fiber diameter of WSL system 43

4.15 Relation between applied voltage and average fiber diameter of BSL system 43

4.16 SEM image of BSL 45% solution electrospun at 20cm 20kV (a), 25cm 20kV (b) 45

4.17 SEM images of carbon fiber produced from lignin fiber: CKL system 15cm 15 kV (a), 15cm 20 kV (b), BSL system 25cm 10 kV (c), 25cm 20 kV (d) 46

CHAPTER I

INTRODUCTION

In pulp, paper and wood chip industry the important and most abundant waste is bark. Bark containing in wood is about 18% of total weight of the wood [1]. Nowadays most of bark is used as a fuel for producing steam and electricity. In Thailand, most of feedstock of the industries is eucalyptus wood which is classified in hardwood type.

Lignin is the second most abundant natural substance in the world after cellulose. The major source of lignin is black liquor which obtained from pulp industry. With great availability, complex molecular structure and interesting properties of lignin, lignin can be used as feedstock instead of fossil based compound. Many potential opportunities for adding value to lignin have been reported by Pacific Northwest National Laboratory [2] such as;

- Use as heat source for the process for example direct burning as in pulp mill (black liquor), use as feed stock for syngas via gasification which can be used for producing chemicals such as DME, Methanol, etc
- Use as polymer additive
- Use as precursor in production of aromatic compound such as BTX, cyclo hexane, etc.
- Lignin is suitable displacing synthetic polymers such as polyacrylonitrile (PAN) in the production of carbon fiber

Carbon fibers are materials which have good properties [3]. They generally have excellent tensile property, low density, high thermal and chemical stability, good thermal and electrical conductivity and excellent creep resistance. Nowadays, the carbon fibers are being used in different industries such as aerospace, military, turbine blade, construction, light weight cylinder and vessel, automobile, medical, sports, etc. In automobile industry, carbon fiber composite polymer offers light weight and superior styling which can be found in body part, door, drive shaft, etc.

Most of the current carbon fiber market is produced from PAN while the rest is pitch and others [3]. Different precursors produce carbon fibers with different properties and require different process conditions. However, the essential features are very similar. Generally, carbon fibers are produced by a controlled pyrolysis. Precursor fibers are stabilized at 200^{o}C – 400^{o}C in air and followed by carbonization at 1000^{o}C under nitrogen atmosphere to remove hydrogen, oxygen and other non carbonaceous elements.

PAN is an excellent precursor for producing carbon fibers. It has been widely studied and is in commercial production. However, PAN is expensive. Alternative sources of precursor have been widely studied. Lignin is one of the alternatives. With its high molecular weight polyaromatic macromolecule, it has been widely studied to be used as a precursor for carbon fiber production. Kubo et al. [4] first reported the use of commercial lignin as a precursor for carbon fiber utilizing a thermal extrusion process.

Electrospinning is a well known process to produce a highly impermeable, nonwoven fabric of nanometer to micron diameter fibers from polymer solution by pushing a millimeter diameter liquid jet through a nozzle with an electric field. In conventional view, electrostatic charging of the fluid at the tip of the nozzle results in the formation of the well known Taylor cone, from the apex of which a single fluid jet is ejected. As the jet accelerates and thins in the electric field, radial charge repulsion results in splitting of the primary jet into multiple filaments. As the jet travels in air, the solvent evaporates, leaving a charged fiber behind which lays itself randomly on a collecting metal screen. Thus, continuous fibers are laid to form a non-woven fabric [6]. Studies on electrospinning of technical lignin have been reported by Dallmeyer et al [7].

In hardwood bark, lignin composition is about 40 – 50 % [1]. Bark lignin has been studied for using as raw material for adhesive. The possibility of replacing phenol in PF resin with lignin was also explored [8].

In this work, eucalyptus woodchips and its bark were collected from woodchip mill and used as sources of lignin. Regarding to the safety issue, soda pulping process was used for extraction of lignin from the raw material instead of Kraft process. The electrospinning technique was used for producing carbon fibers from three different types of lignin which are Commercial Kraft lignin, Bark Soda lignin and Wood soda lignin using DMF as solvent. PEO was used to facilitate the fiber formation. Lignin fibers were then stabilized and carbonized. Due to the availability of eucalyptus bark, we aimed to find the possibility to use the bark lignin as a precursor of carbon fiber. There are several reports to produce carbon fibers from several types of lignin. To the best of our knowledge, it is the first report on producing of carbon fiber from bark lignin by electrospinning method.

Aim of this study is to understand the effluence of various effects of various process parameters such as % concentration of lignin, applied voltage, working distance, optimum condition for electrospinning, addition of PEO, as well as the sources of lignin on morphology, size distribution of lignin fiber and lignin carbon fiber.

Objectives of the research:

1. To prepare lignin from Eucalyptus bark by Soda pulping process
2. To synthesis lignin fiber by electrospinning technique and lignin carbon fiber by stabilization and carbonization of lignin fiber
3. To investigate size, morphology of difference sourced lignin fiber and carbon fiber.

The present study is arranged as follows:

Chapter I is the introduction of this work

Chapter II described the basic theory about lignin, pulping process, carbon fibers, electrospinning process, literature survey of previous works related to this research is also presented in this chapter.

Chapter III shows materials, the experimental equipments, the extraction of lignin by Soda pulping process, electrospinning process, stabilization and carbonization process and characterization equipment.

Chapter IV describes the results and discussion of the research.

In the last chapter, the overall conclusions of this research and future work are given.

CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Lignin

2.1.1 Structure of lignin

Lignin [2] is a natural amorphous polymer made up of substituted aromatic structures. At the highest level, two types of lignin are recognized: 1) native lignin, which is lignin as it is present in biomass, and 2) technical lignin, which is lignin isolated from biomass through various processes. Several lignin review articles detail various areas of lignin structure, both native and technical. The following overview will illustrate how lignin's structure leads to processing challenges. These challenges differ significantly from those presented by more homogeneous feedstocks such as sugars.

Lignin is considered the essential natural glue that holds all plants together. More specifically, lignin is a natural amorphous polymer made up of randomly branched and cross linked aromatic units. Through crosslinking with cellulose carbohydrates, lignin confers strength, rigidity and flexibility as well as aiding in water transport and imparting a measure of protection against attack by marauding insects and microorganisms. Many structures have been proposed for lignin as it is found in nature (so-called "native" lignin). Any of these structures are approximations at best since lignin's structure is not identical for all varieties of plants. In addition, methods used for lignin extraction and isolation frequently modify its native structure. The composition, molecular weight and even the amount of lignin available also differ by plant source. Generally, the abundance of lignin in biomass decreases in order from softwoods > hardwoods > grasses (Table 2.1).

Table 2.1: Percentage of lignin in various biomass sources

Source	% lignin
Softwoods	27 – 33
Hardwoods	18 – 25
Grasses	17 - 24

Regardless of its complexity, lignin's unifying structural feature is a branched and crosslinked network of C9 phenylpropenyl units. Biosynthetically, these C9 units are provided by the enzymatic dehydrogenative polymerization of coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Coniferyl and sinapyl alcohol are the starting points for the formation of the well-known guaiacyl and syringyl structures of lignin (Figure 2.1).

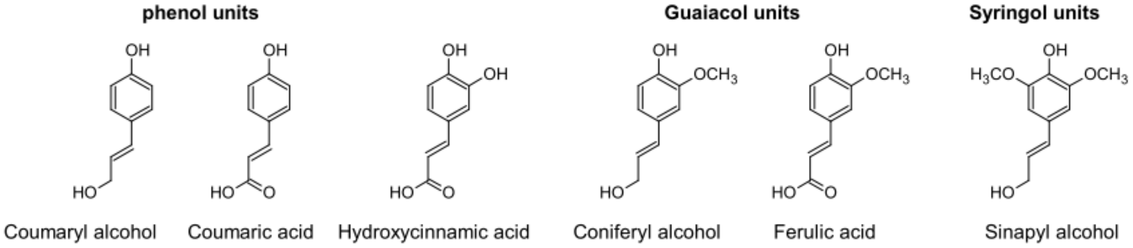


Figure 2.1: Types of C9 units found in lignin

Table 2.2 shows the relative proportion of these units depends on the lignin source. Softwoods are made up of guaiacyl units, whereas hardwoods contain both guaiacyl and syringyl units. Grasses additionally contain a variety of acidic guaiacyl units attached as esters and exhibit further substitution of p-coumaryl alcohols with p-coumaric, hydroxycinnamic, and ferulic acids. Softwood lignin is generally higher in molecular weight than hardwood lignin.

Table 2.2: Lignin compositions by source

Source	Composition
Softwoods	Primarily derived from coniferyl alcohol (90%) with the remainder derived from p-coumaryl and sinapyl alcohol
Hardwoods	Approximately equally derived from coniferyl and synapyl alcohols
Grasses	Primarily derived from coniferyl and sinapyl alcohols with 10 – 20% p-coumaryl alcohol.

Trifunctionally linked units also provide numerous branching sites and ring units. Figure 2.2 illustrates a hypothetical structure for a native softwood lignin based on estimates of the proportions of these substructural units.

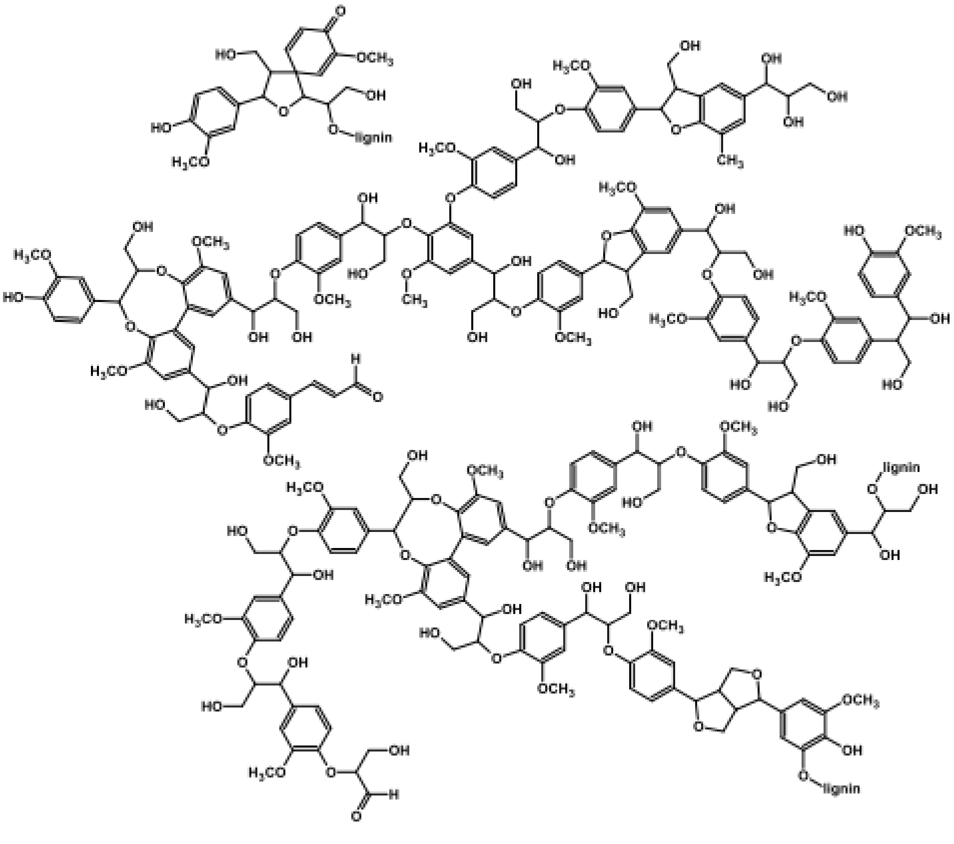


Figure 2.2: General structure of native lignin

2.1.2 Technical lignins

The "technical lignin" [23] arising from such methods has undergone severe hydrolytic degradation imparting a highly reactive structure and a relatively low molecular weight. This can render technical lignin unsuitable for many value added applications despite its aromatic and somewhat polymeric nature.

Technical lignins have diverse properties allowing for a broad range of applications. These applications require lignin with tailored properties: molecular weight, purity, homogeneity, and the presence of function groups. The major chemical properties of technical lignins are shown in Table 2.3.

Table 2.3 Chemical properties of the technical lignins [23]

Parameter	SL	KL	HL	OSL	LS	ILL
Ash, %	0.7 – 2.3	0.5 – 3.0	1.0 – 3.0	1.7	4.0 – 8.0	0.6 – 2.0
Moisture,%	2.5 – 5.0	3.0 – 6.0	4.0 – 9.0	7.5	5.8	-
Acid soluble lignin,%	1.0 – 11	1 – 4.9	2.9	1.9	-	-
Nitrogen, %	0.2 – 1.0	0.05	0.5 – 1.4	0 – 0.3	0.02	-
Sulphur, %	0	1.0 – 3.0	0 – 1.0	0	3.5 – 8.0	1.5
Molecular weight	1,000 – 3,000	1,500 – 5,000	5,000 – 10,000	500 – 5,000	1,000 – 50,000	2,000

SL = Soda lignin, KL = Kraft lignin, HL = Hydrolysis lignin, OSL = Organosolv lignin, LS = Lignosulphonates, ILL = Ionic liquid lignin

2.2 Alkaline processes and lignin precipitation

In the alkaline process [25], lignocellulosic material is treated with sodium hydroxide or ammonia. The alkaline pretreatments are applied to a variety of lignocellulosic substrates, primarily to increase their digestibility for feeding to ruminants. This treatment is also used in alkaline pulping processes (soda and Kraft). In the soda pulping process, wood is treated hot sodium hydroxide solution under pressure. The Kraft or sulfate pulping process uses a NaOH – Na_2S mixture (white liquor) to dissolve lignin from wood carbohydrates.

Kraft pulping is the dominant chemical pulping process in the world. The process is conducted at high pH in the presence of substantial amounts of aqueous sulfide, sulfhydryl and polysulfide and at temperatures in the range of 150-180 ºC for around two hours. However, in this study used soda process for extracting of lignin.

Lignin may be recovered from the black liquor by lowering the pH. Typically, this is done with carbon dioxide or with mineral acids. On lowering the pH, a substantial portion of the lignin is precipitated and may be recovered by filtering and washing. Given the high-sulfur environment of kraft pulping, the sulfur content of precipitated and washed kraft lignin is surprisingly quite low, typically less than 1-2% which is consistent with the number of –SH linkages created during the kraft pulping process. But for soda lignin sulfur content is zero because of the pulping process has no Na_2S.

It has been reported by Oak Ridge National Laboratory (ORNL) that the reasons of spinning (melt) difficulties are from particulate contaminants, hemicelluloses and voids formed. They have proposed the solution, shown in Table 2.4, to solve those problems.

Table 2.4 Solution to spinning problems

Problem	Solution
Particulates and fiber block spinnerettes	Prefilter black liquor prior to lignin preparation
Voids formed by water vapor	Minimize water uptake by prompt processing or proper packing. Remove hemicllulose carbohydrate which chemically binds water.
High ash content of commercial lignins and pulping liquors	Desalt by washing lignin powder or gel with distilled or deionized water.

ORNL reported the method to remove hemicelluloses and lignin from black liquor by fractional precipitation. The higher pH range about 9.8 - 10 spans hemicelluloses precipitation, the lower range about 3.5 - 4, lignin precipitation from a filtered, hemicelluloses-stripped liquor.

2.3 Physical properties of carbon fiber

Carbon fiber is defined as a fiber containing at least 92 wt % carbon, while the fiber containing at least 99 wt % carbon is usually called a graphite fiber [3]. Carbon fibers generally have excellent tensile properties, low density, and high thermal and chemical stabilities in the absence of oxidizing agents, good thermal and electrical conductivities, and excellent creep resistance. They have been extensively used in composites in the form of woven textiles, prepregs, continuous fibers/rovings, and chopped fibers. The composite parts can be produced through filament winding, tape winding, pultrusion, compression molding, vacuum bagging, liquid molding, and injection molding.

The atomic structure of a carbon fiber is similar to that of graphite, consisting of carbon atom layers (graphene sheets) arranged in a regular hexagonal pattern, as shown in Figure 2.3. Depending upon the precursors and manufacturing processes, layer planes in carbon fibers may be either turbostratic, graphitic, or a hybrid structure.

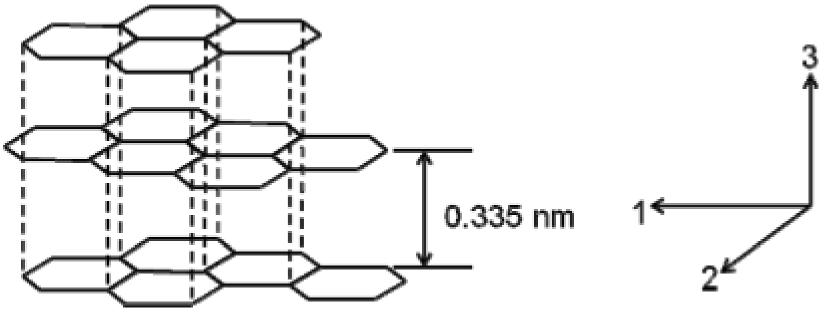


Figure 2.3 Structure of graphitic crystals

2.4 Electrospinning

Although the term ‘‘electrospinning’’ [25] , derived from ‘‘electrostatic spinning’’, was used relatively recently (in around 1994), its fundamental idea dates back more than 60 years earlier. From 1934 to 1944, Formalas published a series of patents describing an experimental setup for the production of polymer filaments using an electrostatic force. In electrospinning [16], a high voltage is applied to a polymer fluid such that charges are induced within the fluid. When charges within the fluid reached a critical amount, a fluid jet will erupt from the droplet at the tip of the needle resulting in the formation of a Taylor cone. The electrospinning jet will travel towards the region of lower potential, which in most cases, is a grounded collector. There are many parameters that will influence the morphology of the resultant electrospun fibers, from beaded fibers to fibers with pores on its surface. Although electrospinning has been carried out on molten polymer but most electrospinning are carried out using polymer solution.

The standard laboratory setup for electrospinning consists of a spinneret (typically a hypodermic syringe needle) connected to a high-voltage (5 to 50 kV) direct current power supply and a grounded collector. Figure 2.4 shows the basic schematic of the electrospinning.

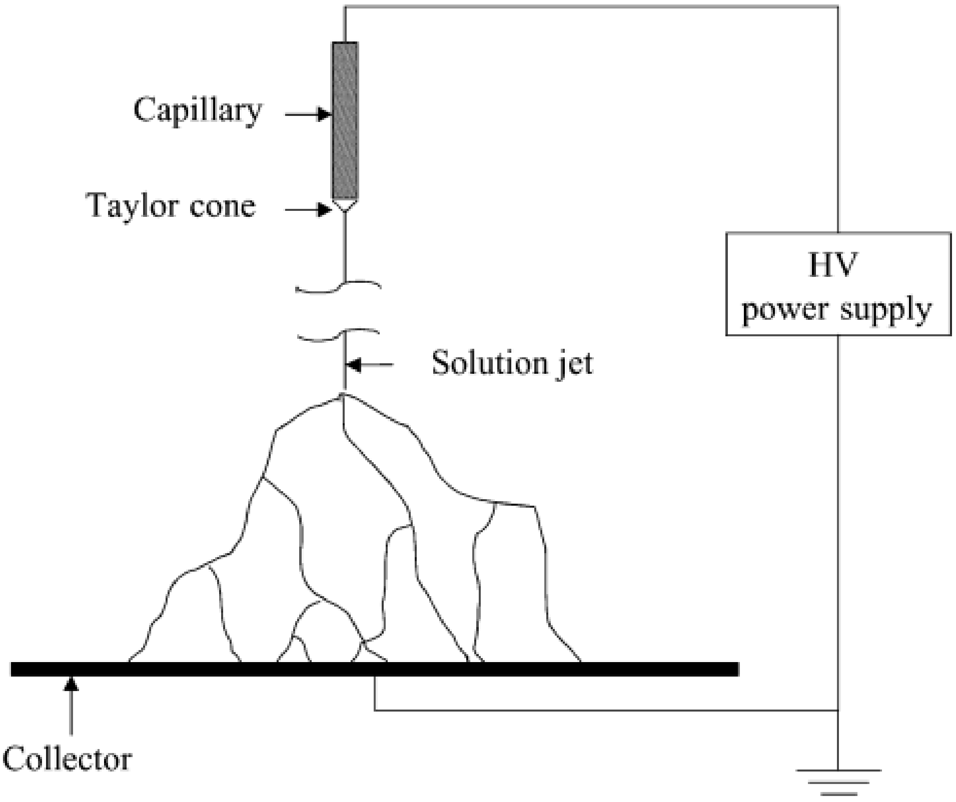


Figure 2.4: Scheme for electrospinning equipment

The parameters affecting electrospinning and the fibers may be broadly classified into polymer solution parameters, processing and ambient conditions [16]. With the understanding of these parameters, it is possible to come out with setups to yield fibrous structures of various forms and arrangements. It is also possible to create nanofiber with different morphology by varying the parameters.

- **Polymer Solution Parameters**

The properties of the polymer solution have the most significant influence in the electrospinning process and the resultant fiber morphology. The surface tension has a part to play in the formation of beads along the fiber length. The viscosity of the solution and its electrical properties will determine the extent of elongation of the solution. This will in turn have an effect on the diameter of the resultant electrospun fibers.

- **Processing Conditions**

Another important parameter that affects the electrospinning process is the various external factors exerting on the electrospinning jet. This includes the voltage supplied, the feed rate, temperature of the solution, type of collector, diameter of needle and distance between the needle tip and collector. These parameters have a certain influence in the fiber morphology although they are less significant than the solution parameters.

- **Ambient Parameters**

The effect of the electrospinning jet surrounding is one area which is still poorly investigated. Any interaction between the surrounding and the polymer solution may have an effect on the electrospun fiber morphology. High humidity for example was found to cause the formation of pores on the surface of the fibers. Since electrospinning is influenced by external electric field, any changes in the electrospinning environment will also affect the electrospinning process.

Important features of electrospinning should comply with the following guideline:

- Suitable solvent should be available for dissolving the polymer.

- The vapor pressure of the solvent should be suitable so that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range.
- The viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette.
- The power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette.
- The gap between the pipette and grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form.

There are many researcher have tried to find the new precursor for carbon fiber which is cheap, high carbon content and natural base. Most of the research focus on Lignin because it is phenolic compound and huge available in natural.

Most of previous research, the researcher used a melt spinning technique to produce carbon fiber from lignin. The lignin is melted and pumped through a spinneret (die) with numerous holes (one to thousands). The molten fibers are cooled, solidified, and collected on a take-up wheel. Several paper were published, In 1969, Otani [26] published a patent for producing carbonized lignin fiber. Sudo et al. also produced carbon fibers from lignin with fairly good mechanical properties by breaking intermolecular interactions through modifying hydroxyl and hydroxy methyl groups.

Sano et al. [27] reported a process of producing carbon fibers from an organosolv lignin. The lignin is obtained from birch wood by an aqueous acetic acid pulping process. Organosolv lignin is much purer than the commercial kraft lignin. Once removing the volatile components, the lignin shows nice melt spinnability. The carbon fibers with a 14 ± 1 μm diameter showed tensile strength of about 355 MPa and modulus of about 39.1GPa.

Kadla et al. [28] produced carbon fibers from an Organosolv lignin, a softwood Kraft lignin and a softwood Kraft lignin, and blends of lignin and poly(ethylene oxide) (PEO). The Kraft lignin was first purified or desalted by repeated washing using distilled water while keeping the pH below 5 with HCl till the salt was less than 1,000 ppm. Precursors were then extruded at temperatures between 130 °C and 240 °C depending on the fiber blend. It was shown that PEO was miscible with the lignin and facilitated the fiber spinning. The precursor fibers were then stabilized at temperature up to 250 °C in air at various heating rate (12 -180^{o}C/h) and carbonized in nitrogen at the final temperature of 1,000°C at heating rate (180^{o}C/h). The carbon yield was between 40%–46%. However, hardwood Kraft lignin/PEO blends with greater than 5% PEO, and all Alcell lignin/PEO blends were thermally unstable and displayed inter-fiber fusing during carbonization. The mechanical properties, tensile strength and the modulus, increased with decreasing fiber diameter. The resultant of carbon fibers with diameter of 31–63 μm were in the range of 400–550 MPa and 30–60 GPa, respectively.

Kubo and Kadla [5] produced carbon fibers from hardwood lignin/synthetic polymer blend fibers. Hardwood Kraft lignin was thermally blended with two recyclable polymers, poly(ethylene terephthalate) (PET) and polypropylene (PP) using a similar process as described above. DSC analysis of the precursor fibers revealed that the lignin/PET blends are miscible while the lignin/PP blends are immiscible. Blending with PET enabled higher heating rates to be used and dramatically improved the thermal stability of the resulting polyblend fibers. Upon blending with PET, the mechanical properties of the carbon fibers increased slightly. For the precursor with a lignin/PET ratio of 75/25, the resultant carbon fibers with a diameter of about 34 ± 5μm showed modulus of 94 GPa and tensile strength of about 703 MPa.

Kadla et al. [29] also studied the stabilization of lignin precursor fibers in air at various constant heating rates by building a continuous heating transformation diagram. A heating rate of 0.06 °C/min was required to ensure Tg above the temperature of the heating medium. Elemental analysis revealed that carbon and hydrogen content decreased in the whole stabilization step while the oxygen content increased at temperatures of up to 200–250 °C and then decreased at higher temperature.

For sub micron lignin carbon fiber produced from Electrospinning technique, several researches are available. Lallave et al.[30] reported the manufacture of carbon nanofibers from lignin. They formulated a method by which an organosolv lignin (Alcell) dissolved in ethanol at ratios around 1: 1w/w. Lignin fibers were in the range of 400 nm to 2 mm diameter. Difficulties caused by the evaporation of ethanol from the highly concentrated solution led to the use of a coaxial spinneret whereby ethanol was passed through an outer sheath to prevent Taylor Cone solidification. Oxidative thermostabilization of the thermoplastic lignin fibers was brought about by a heat treatment in air consisting of a ramp phase to 200^{o}C at 0.25^{o}C/min, and an isothermal phase of 24 h, while carbonization to 900^{o}C was achieved at 10^{o}C/min. Carbon nanofibers were recovered in 31.6% yield (based on the initial nanofiber). The fiber had diameters of 200 nm, and had surface areas of up to 1200 m^{2}/g (BET, N_2). Further to this, the use of a tri-axial spinneret, which added a center hole through which glycerin could be pumped, led to the preparation of lignin nanotubes, which could be oxidatively thermostabilized at a rate of 0.05^{o}C/min to 200^{o}C, and carbonized at a rate of 10^{o}C/min to 900^{o}C, to give carbon tubes of 400 nm diameter.

Dallmeyer et al. [7] reported the electrospinning of seven different technical lignins including Softwood kraft lignin, hardwood kraft lignin, sulfonated kraft lignin, hardwood organosolv lignin, softwood organosolv lignin, pyrolytic lignin and lignosulfonate, used single orifice method. They reported that none could be electrospun without substantial bead formation unless a small amount of poly(ethylene oxide) was added. The addition of just 1% (w/w) PEO enabled the continuous electrospinning of micron sized fibers, and further adjustments of lignin concentration enabled the production of submicron diameter fibers from each lignin. However, the conversion properties of the lignin fibers have not yet been reported.

Similarly, Seo et al.[31] reported the electrospinning of PAN/lignin (alkali type) composite submicron fibers. Solutions comprising between 100: 0 and 80 : 20 w/w PAN/lignin were electrospun under identical conditions to give fibrous mats of varying morphology. In this case oxidative thermostabilization was brought about by electron beam irradiation rather than by thermal ramping, and carbonization was effected by thermal treatment to 1000^{o}C at a rate of 10^{o}C/min, to give fairly uniform fibers of 300nm average diameter. The authors monitored the tensile strength of the spun fiber mats during stabilization as a function of irradiation dose to determine appropriate irradiation levels. The best performing carbon fiber mats were produced using a 50 : 50 PAN/lignin solution, 15kV, and with a target distance of 100mm to manufacture the fiber mat; and a radiation dose of 2000 kGy to render the fibers infusible prior to carbonization. The latter process could have potential significance if applied to the conversion of melt spun low T_g lignin fiber to carbon fiber.

CHAPTER III

EXPERIMENTAL

This chapter describes the experiment procedures for lignin extraction and fibers production. It is divided into four parts: materials used, electrospinning apparatus, experimental procedures and samples characterizations.

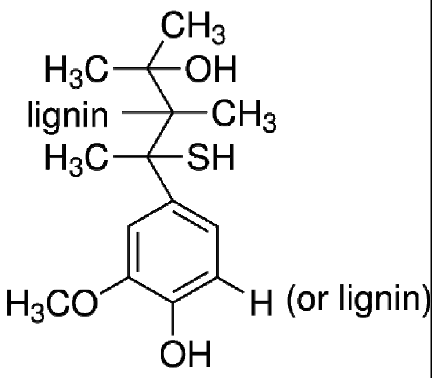
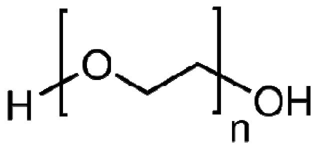
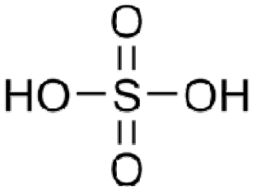
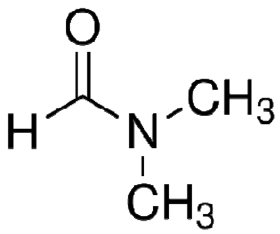
3.1 Materials

List of chemicals employed in this work and their structures are listed in Table 3.1 and 3.2 respectivelt.

Table 3.1 List of chemical agents used in the research

Chemical agent	Used for	Manufacturer/Grade
Sodium hydroxide (NaOH)	Lignin extraction/ Soda pulping process	LOBA Chemie, 98%
Lignin, alkali	Synthesis of Carbon fiber	Aldrich
Poly(ethylene oxide), average Mv = 600,000 $H-(O-CH_2-CH_2)_n-OH$	Polymer blender	Aldrich, 99%
Sulfuric acid (H_2SO_4)	Precipitation of lignin	Fisher, 95.00%
N,N-Dimethylformamide ($HCON(CH_3)_2$)	Solvent	Fisher, 99.99%
Distilled water	Lignin extraction	
Eucalyptus Bark	Lignin extraction	Shaiyo-AAA Co.,Ltd.
Eucalyptus woodchip	Lignin extraction	Shaiyo-AAA Co.,Ltd.

Table 3.2 Chemical structure of compound used in this research

Chemical name	Designation	Chemical structure
Sodium hydroxide (NaOH)	NaOH	
Lignin, alkali	CKL	
Poly(ethylene oxide), average Mv = 600,000 H-(O-CH_2-CH_2)$_n$-OH	PEO	
Sulfuric acid (H_2SO_4)	S	 $HO-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-OH$
N,N-Dimethylformamide ($HCON(CH_3)_2$)	DMF	

3.2 Pulping Apparatus

The schematic of the pulping apparatus used in this work is shown in Figure 3.1. The components of the apparatus and their functions are described as follows.

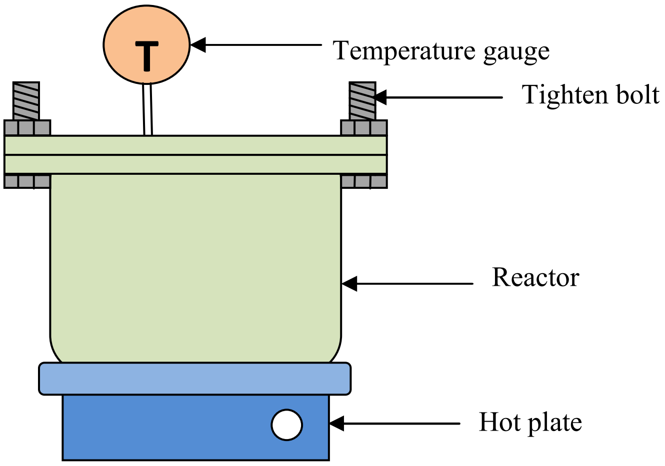


Figure 3.1 Schematic of pulping setup

The system is consisted of:

- A 2000 mL stainless steel reactor with fastening bolt and sealing
- A hot plate was used for heating the reactor
- A temperature gauge range of 0 – 300°C was used for measuring the solution temperature

3.3 Electrospinning Apparatus

The schematic of the electrospinning apparatus used in this work is shown in Figure 3.2. The components of the apparatus and their functions are described as follows.

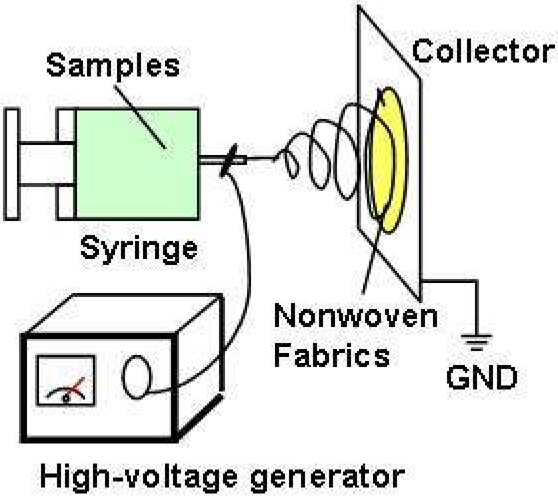


Figure 3.2 Schematic of electrospinning setup

The system is consisted of:

- A high-voltage power supply (Protek, DF 1730SB3A, UAS) was used to generate either positive or negative DC voltage up to 30 kV
- A 20 ml syringe was used as a container for electrospinning solution. The syringe is made of a glasses and set of 45 degree
- A stainless steel needle (gauge No.19) was used as a nozzle. The tip was cut into a flat shape and the length of the needle was 10 mm. The needle is connected to the negative electrode of DC supply.
- Aluminum foil was used as a ground collctor.

3.4 Experimental procedure

3.4.1 Material preparation

Commercial Kraft lignins (CKL) were used as received. Eucalytus bark and wood chip were used as a raw material for Bark Soda lignin (BSL) and Wood Soda lignin (WSL) respectively.

3.4.2 Lignin extraction

The delignification of bark and woodchip were performed in 2000 ml stainless steel reactor equipped with temperature gauge. The hot plate was used for heating the reactor. 1000 ml of 5 mol/l Sodium hydroxide solution and 150 g of bark or woodchip were taken in the reactor. Delignification was carried out for 5 h at 170^{o}C.

3.4.3 Lignin precipitation

The black liquor was then filtered and the soda lignin was precipitated from the concentrated black liquor by titration to lower pH using 50% concentration of Sulfuric acid. The titration was separated to be two times. The filtered black liquor was stirred in a beaker and sulfuric acid was added drop wise. After pH was reduced to 8 – 9, stirring was stopped and the precipitate allowed to settle. The hemicellulose was then removed by filtration. When filtration was finished, Lignin was then prepared from the filtrate. Lignin was prepared from hemicelluloses stripped black liquor by direct precipitation with sulfuric acid. The weak black liquor was stirred in a beaker and sulfuric acid was added drop wise. After pH was reduced to 2 – 4, stirring was stopped and the precipitate was allowed to settle. The precipitated lignin was then filtered and washed by distilled water with keeping the pH below 4. The obtained soda lignin was then dried in an oven at 60^{o}C.

3.4.4 Solution preparation

Electrospinning solutions were prepared as follows: The appropriate amounts of lignin (CKL, BSL, and WSL) and PEO were weighted as the desired fraction. The appropriate volume of solvent (DMF) was then added to reach the desired total polymer concentration in the range of 35 – 55wt%. The solutions were then stirred by magnetic stirrer for 2 hours. Because the solutions were optically opaque, the mixing was evaluated by qualitative observation of the flow behavior inside the vial containing the solution to ensure that there were undissolved solids.

3.4.5 Electrospinnning

Electrospinning was carried out in a 45 degree orientation using 20 ml glasses syringe fitted with 18G needle as a spinneret connected to the positive terminal of a high voltage power supply. The operating voltage was varied from 10 – 20 kV. An aluminum foil collector was placed 10 -25 cm from the spinneret and was connected to ground.

3.4.6 Thermostabilization and Carbonization

The lignin fibers were thermostabilized in a tubular furnace under the air atmosphere (150 cm^3 STP/min of air). The fibers were heated from room temperature up to 250^oC at heating rate of $50^oC/hr$, maintaining the final temperature (250^oC) for 1 hr. The stabilized fiber were subsequently carbonized in the same tubular furnace with a flow of N_2 (150 cm^3 STP/min) at $1,000^oC$. the heating rate for carbonization stage was $180^oC/hr$.

3.5 Sample Characterizations

3.5.1 Scanning Electron Microscope

Morphology of the obtained products was studied using scanning electron microscope (SEM) model JSM-6400 at Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Size of the products was then measured from the micrographs, using processing software (JEOL SemAfore 5.21).

3.5.2 Viscosity measurement

Viscosity of the electrospinning solution was measured using a Brookfield Programmable DV II+ viscometer at the Center of Excellence on Particle Technology, Chulalongkorn University. Using small sample adaptor, spindle No.27, fixed stirring speeds at 40 rpm and sample volume 10 ml.

3.5.3 Fourier transform infared spectroscopy (FT-IR)

Function groups of spinning solution were identified by using Fourier transform infrared spectrophotometer (FT-IR) Model Nicolet 6700 at the Center of Excellence on Particle Technology, Chulalongkorn University. The samples were mixed with KBr in a ratio of sample to KBr 1: 300. Infrared spectra were recorded between wave number of 400 and 4000 cm^{-1}.

3.5.4 Thermal gravimetric analysis (TGA)

The decomposition temperature and thermal behavior of the fiber products were studied by using Thermogravimetric analysis on a Mettler-Toledo TGA/DSC1 STARe System at center of Excellence on Particle Technology, Chulalongkorn University. The samples were heated from $25^{o}C$ to $700\ ^{o}C$ under the oxygen flow rate of 40 ml/hr and the ramp rate of $10\ ^{o}C$/min.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, bark lignin extracted from Eucalyptus bark by soda pulping process were investigated. And the lignin fibers fabricated by electrospinning were investigated. And study the influence of various processing parameters and type of lignin on morphology of fibers. Morphology of lignin carbon fibers was investigated.

4.1 Characterization of raw material

4.1.1 FT-IR spectra of lignin

Three technical lignin including Commercial Kraft Lignin (CKL), Wood Soda Lignin (WSL), and Bark Soda Lignin (BSL) were prepared in accordance to the procedure described in chapter III. These three types of lignin were characterized to investigate their functional groups by using FTIR. IR spectrums of lignins are shown in Figure 4.1, 4.2 and 4.3. The summary of IR bonds associated with different types of bonds is shown in Table 4.1.

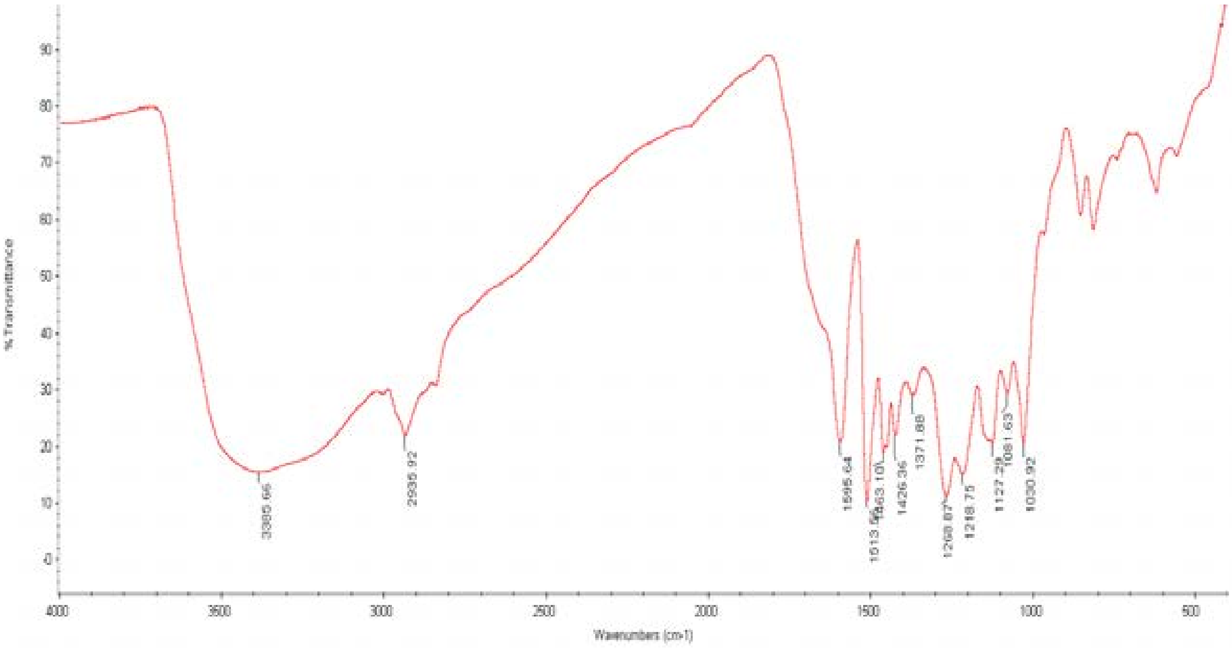


Figure 4.1: FTIR spectrum of commercial kraft lignin (CKL)

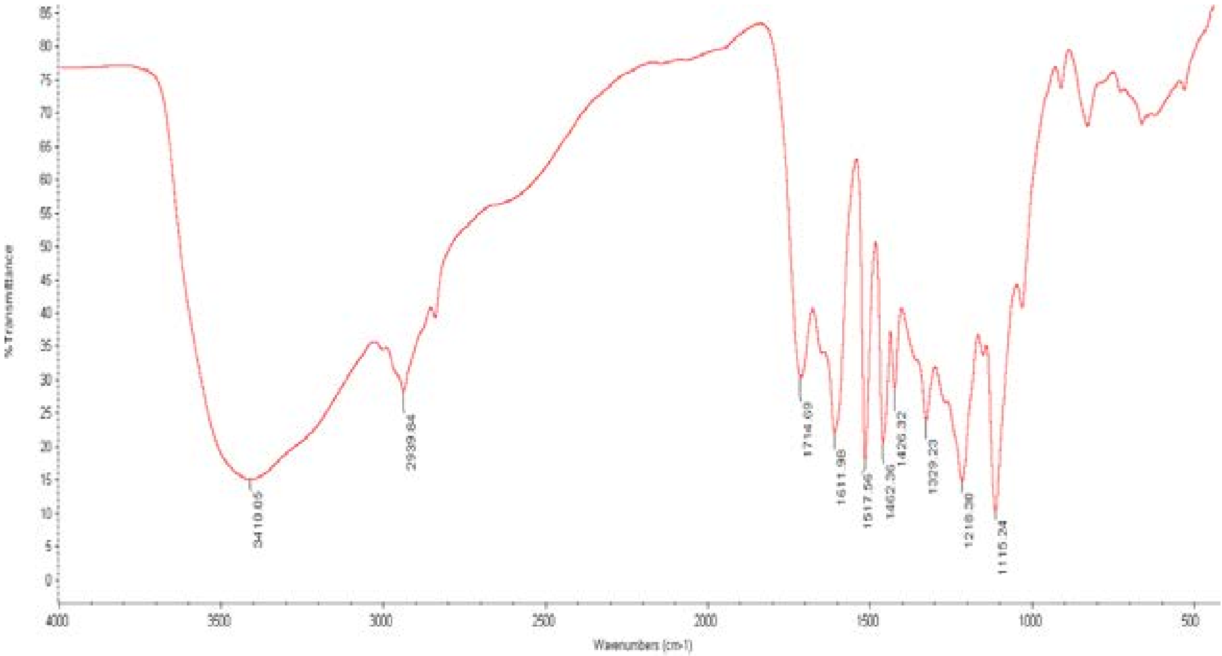


Figure 4.2: FTIR spectrum of wood soda lignin (WSL)

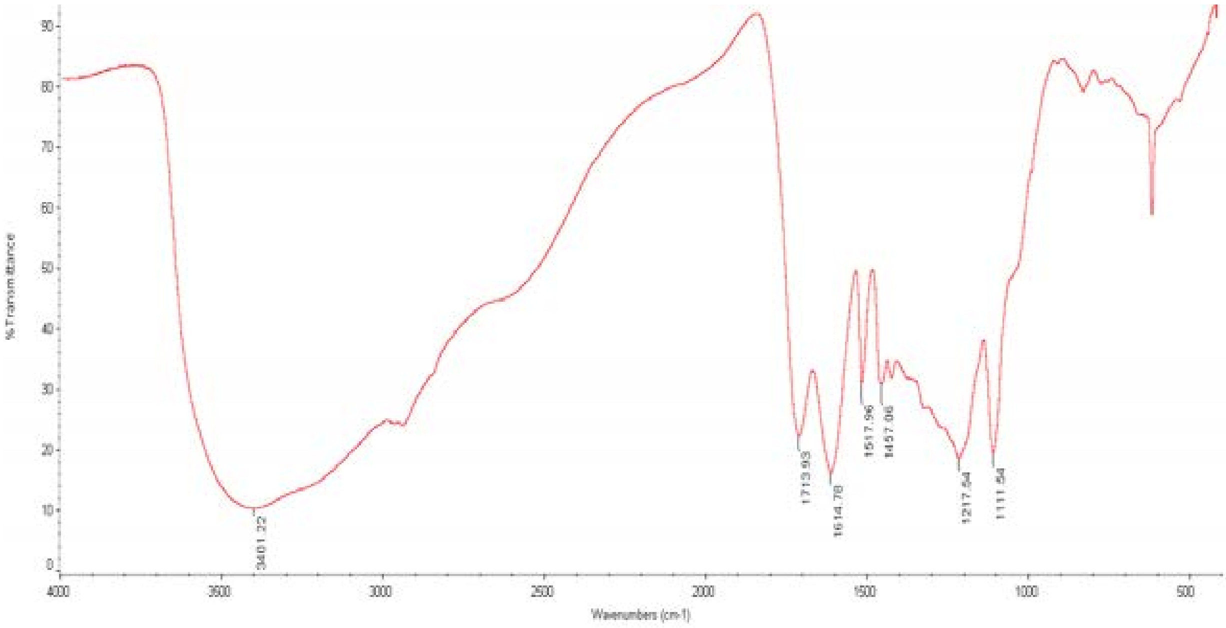


Figure 4.3: FTIR spectrum of bark soda lignin (BSL)

Table 4.1 Summary of IR bands associated with different types of bonds

Band position (cm^{-1})			Assignment	Ref [9][10][11]
CKL	WSL	BSL		
3385.66	3410.05	3401.22	O-H Stretching	Abdul et al., 2011
2935.92	2939.84		C-H Stretching	Abdul et al., 2011
	1714.69	1713.93	C=O Stretching (unconjugated)	Abdul et al., 2011
	1612.29	1614.78	Aromatic skelton vibration +C=O stretching	Abdul et al., 2011
1595.64				Ivan et al., 2008
1513.56	1517.56	1517.96	Aromatic skelton vibration	Abdul et al., 2011
1463.10	1462.36	1457.06	C-H deformation (Methyl and methylene)	Abdul et al., 2011
1426.36	1426.32		C-H in-plane deformation with aromatic ring stretching	Abdul et al., 2011
1371.88			Bending vibration of OH bonds	Jingjing et al.,2011
	1329.23		C-O of syringyl ring	Abdul et al., 2011
1268.87			C-O of guaiacyl ring	Abdul et al., 2011
1218.75	1218.30	1217.54	C-C + C-O stretch	Abdul et al., 2011
1127.29			Deformation vibration of C-H bond in syryngyl rings	Ivan et al., 2008
	1115.24	1111.54	Aromatic C-H in-plane deformation in the syringyl ring	Abdul et al., 2011
1081.63			C-O deformation of secondary alcohols and aliphatic ethers	Abdul et al., 2011
1030.92			C-H deformation in guaiacyl with C-O deformation in the primary alcohol	Abdul et al., 2011

It is well know that the pulping process of wood plays an important role on final structure of lignin. From table 4.1, there were some difference of functional groups between CKL which was produced from Kraft process and WSL which was produced from Soda process.

In the finger print region (1800 and 900 cm^{-1}), the spectral variation were observed in CKL and WSL. The dominating spectra were detected at band positions 1513 cm^{-1} and 1268 cm^{-1}in the CKL for aromatic skeletal vibration and guaiacyl ring breathing. As compared to CKL, the leading peak of WSL was noticed at bands 1517 cm^{-1}, 1218 cm^{-1}, and 1115 cm^{-1}. The relative intensity of band at 1513 cm^{-1} in CKL was stronger than that of the bands 1612 (aromatic skeletal vibration breathing with C=O stretching) and 1462 cm^{-1} (methyl and methylene deformation) of WSL. A sharp intensity of band at 1268 cm^{-1}was exhibited in CKL, and there was no evidence of syringyl transmission at band 1329 cm^{-1}, whereas there was no peak at 1268 cm^{-1}, a strong peak at 1218 cm^{-1}and a syringyl transmission peak at 1329 cm^{-1} were appeared in the WSL. The greater intensity of spectrum at 1463 cm^{-1} was proved the existence of a C-H deformation (Methyl and methylene) CKL. The intensity of spectrum is observed at 1463 cm^{-1} which was equivalent to the band intensity of WSL at 1517cm^{-1}. The transmission peak of guaiacyl type lignin was appeared at about 1268 cm-1, whereas syringyl transmission was visible at band 1329 cm^{-1} in the WSL.

Because WSL is hardwood lignin, the syringyl units are dominating, while guaiacyl units are mainly in CKL which is softwood lignin. This result is well in accordance with the result of the study of properties of softwood and hardwood lignin reported by Abdul and Mohini et al. [9]

In comparison between WSL a BSL, some peaks on BSL were missing. Band at 2939, 1426, and 1329 which were stretching structure missed from the BSL. The relative intensity of band 1614 and 1517 in BSL was stronger than that of band 1612 of WSL. These confirmed the increased concentration of aromatic carbon linkages in the bark lignin. These results is in accordance with the result of the study of comparison between wood lignin and bark lignin of Caribbean pine wood reported by Solar and Kacik et al. [12][13].

4.1.2 Thermal behavior of Lignin

Thermal behaviors of lignin were investigated by Thermal gravimetric analysis. The results are shown in Figure 4.4, 4.5, and 4.6.

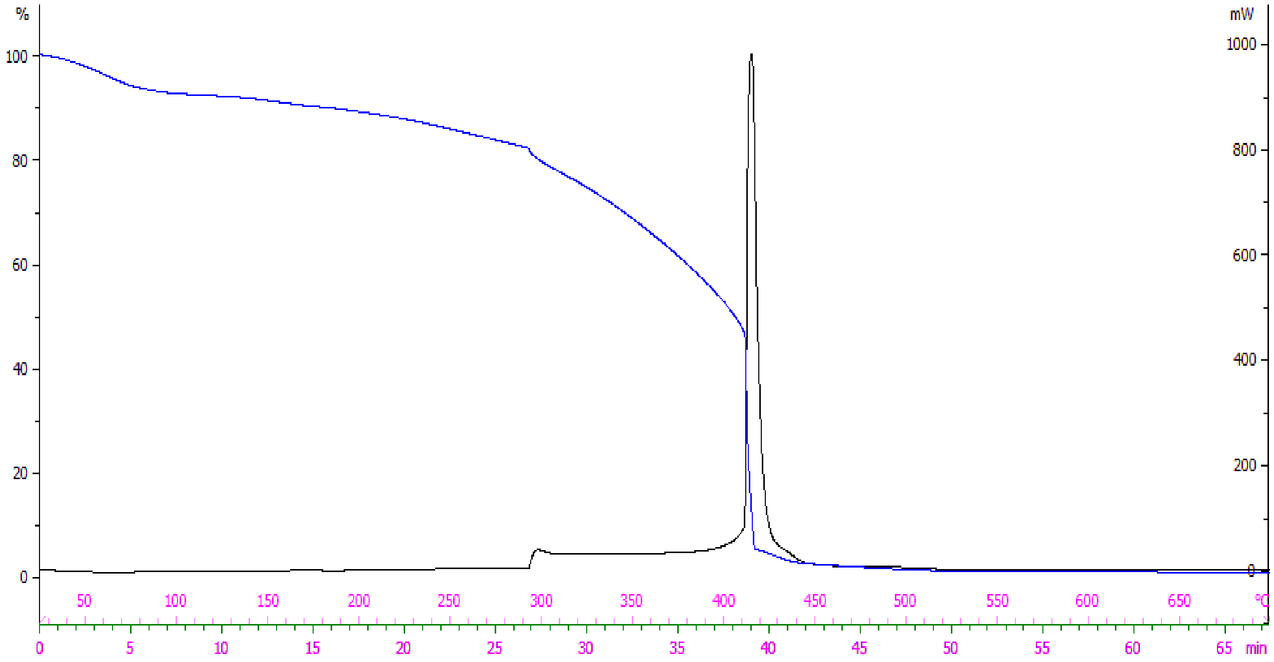


Figure 4.4: Thermal behavior of CKL

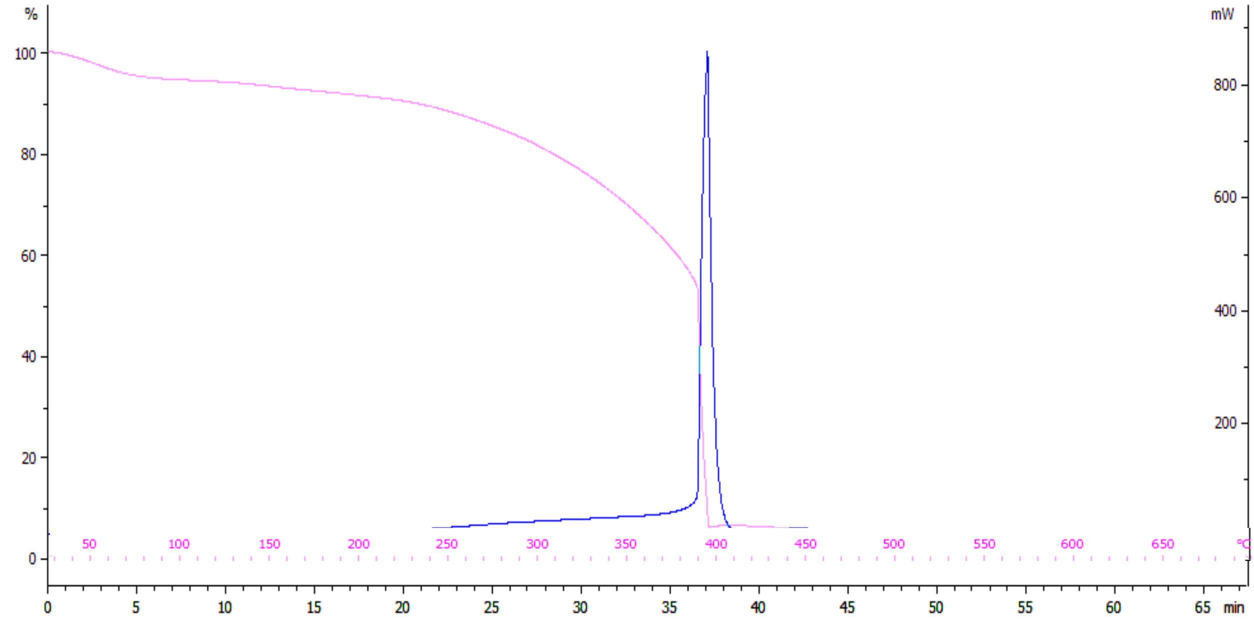


Figure 4.5: Thermal behavior of WSL

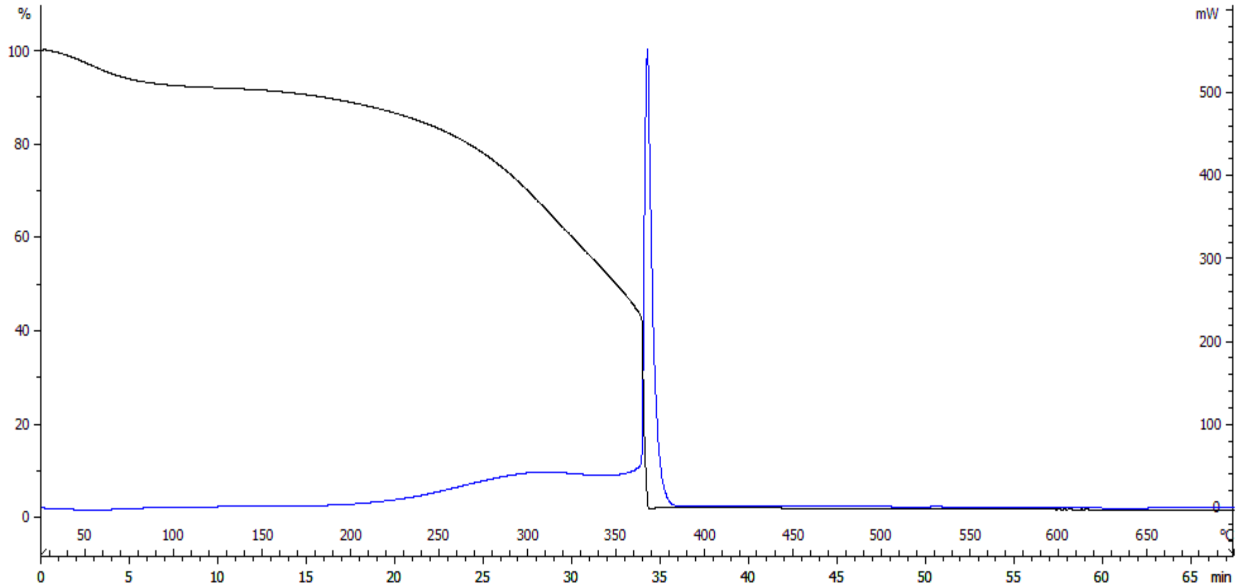


Figure 4.6: Thermal behavior of BSL

The decomposition temperature of CKL, WSL, and BSL are about 415°C, 390°C, and 365°C respectively. The results show that CKL has highest decomposition temperature while WSL is higher than BSL. This means that the softwood decomposes slower than the hardwood and the wood lignin decomposes slower than the bark lignin. These results are in agreement with studies by Abdul et al., 2011 and Solar et al.

It is well known that the decomposition temperature is related with the molecular weight of polymer. The higher the molecular weight is, the higher decomposition temperature becomes [14].

4.1.3 Viscosity of Lignin solution

Three lignin were dissolved in the solvent (DMF) at 40% concentration. Table 4.2 shows the viscosity for the various lignin/DMF solutions.

Table 4.2 Viscosity of Lignin/DMF solution

Lignin	Viscosity at 40% DMF (mPa*s)
CKL	760
WSL	640
BSL	300

Daojie Dong and Arthur L. Fricke [15] reported that increased molecular weight increases viscosity. The molecular weight of the polymer represents the length of the polymer chain, which in turn have an effect on the viscosity of the solution since the polymer length will determine the amount of entanglement of the polymer chains in the solvent [16].

From TGA and viscosity results, we could estimate that the molecular weight of CKL was higher than of WSL and molecular weight of WSL was higher than BSL.

4.2 Effect of solution parameter on electrospinning process

Solutions of each lignin in DMF (CKL, WSL, BSL) were prepared over the concentration range of 40 – 55%wt.. Unfortunately, all samples failed to product fibers. Only electrosprayed droplets were produced, as shown in figure 4.7.

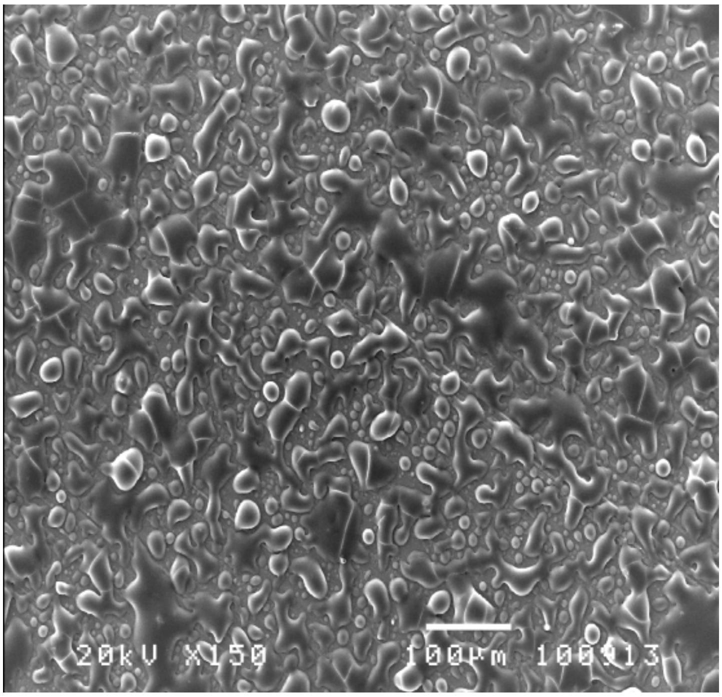
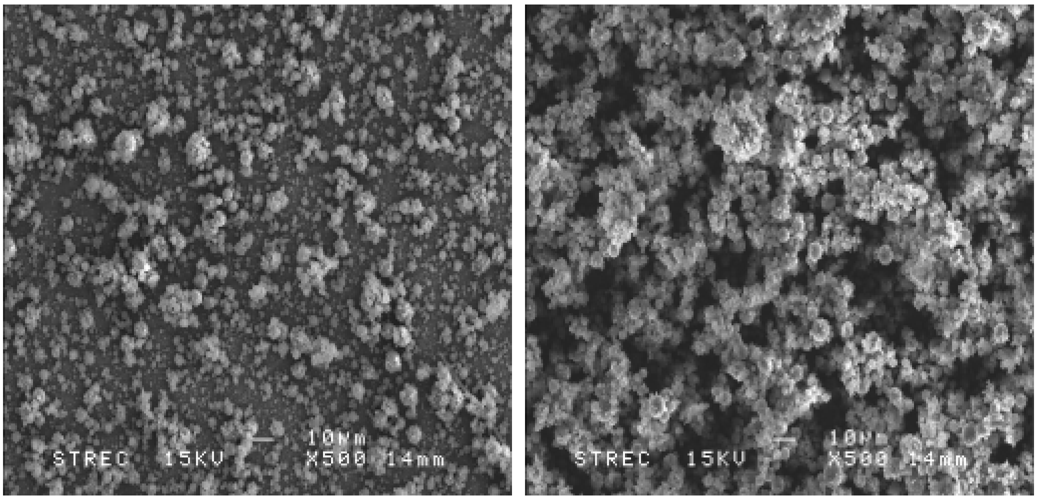


Figure 4.7 SEM image of the droplet on the collector of 50%wt of WSL system

Increased the concentration up to 55%wt of WSL resulted in highly viscous solutions which produced uneven jetting.

Viscosity of solution is the critical key parameter which affects the fiber morphology. It has been proven that continuous and smooth fibers cannot be obtained in very low viscosity, while very high viscosity results in the difficulty ejection of jets. So, optimal viscosity of solution is required for electrospinning.

At 45%wt CKL system displayed visible evidence of beaded fiber formation, figure 4.8a and 4.8b. This resulted was in agreement with the study of electrospinning of technical lignin reported by Dallmeyer et al., [7] Dallmeyer reported that there is a clear concentration dependence on viscosity, wherein all lignin solutions increase in viscosity by an order of magnitude over the range of 30% with exception of softwood kraft lignin which increased by over 2 orders of magnitude. He also reported that the large difference in softwood system may be a result of the difference in the molecular structure and intermolecular interactions.



(a) (b)

Figure 4.8 SEM images of CKL 45% solution electrospun at 15cm, 15kV (a) and 20 cm, 15 kV (b)

It is clear from the previous research [4] that PEO can be used to facilitate the fiber formation. Kadla et al. reported that PEO blend content (<5%) and molecular weight (100–600 K) did not affect the mechanical properties of the carbon fibers. Dallmeyer et al. reported that 1% PEO blend and the solution concentration of 40 wt% as sufficient to form uniform fibers. This is because of PEO has much more molecular weight (600,000 g/mol). Blending only 1% could improve viscoelastic nature of the precursor solution which was due to the formation of hydrogen bonds between the hydroxyl groups of lignin and the ether groups in the PEO backbone [32]. In this work, 1 wt% PEO was added to lignins and dissolved in DMF to reach the solution concentration of 40 wt%. Figure 4.9 shows SEM images of lignin fiber after blended with PEO

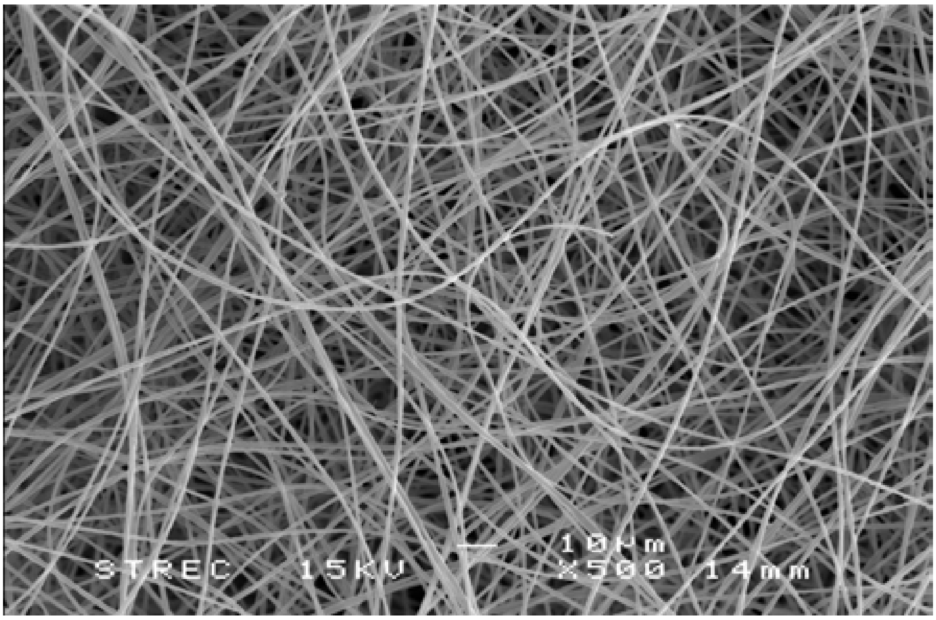


Figure 4.9 SEM image of CKL 40% solution electrospun at 20cm, 20kV

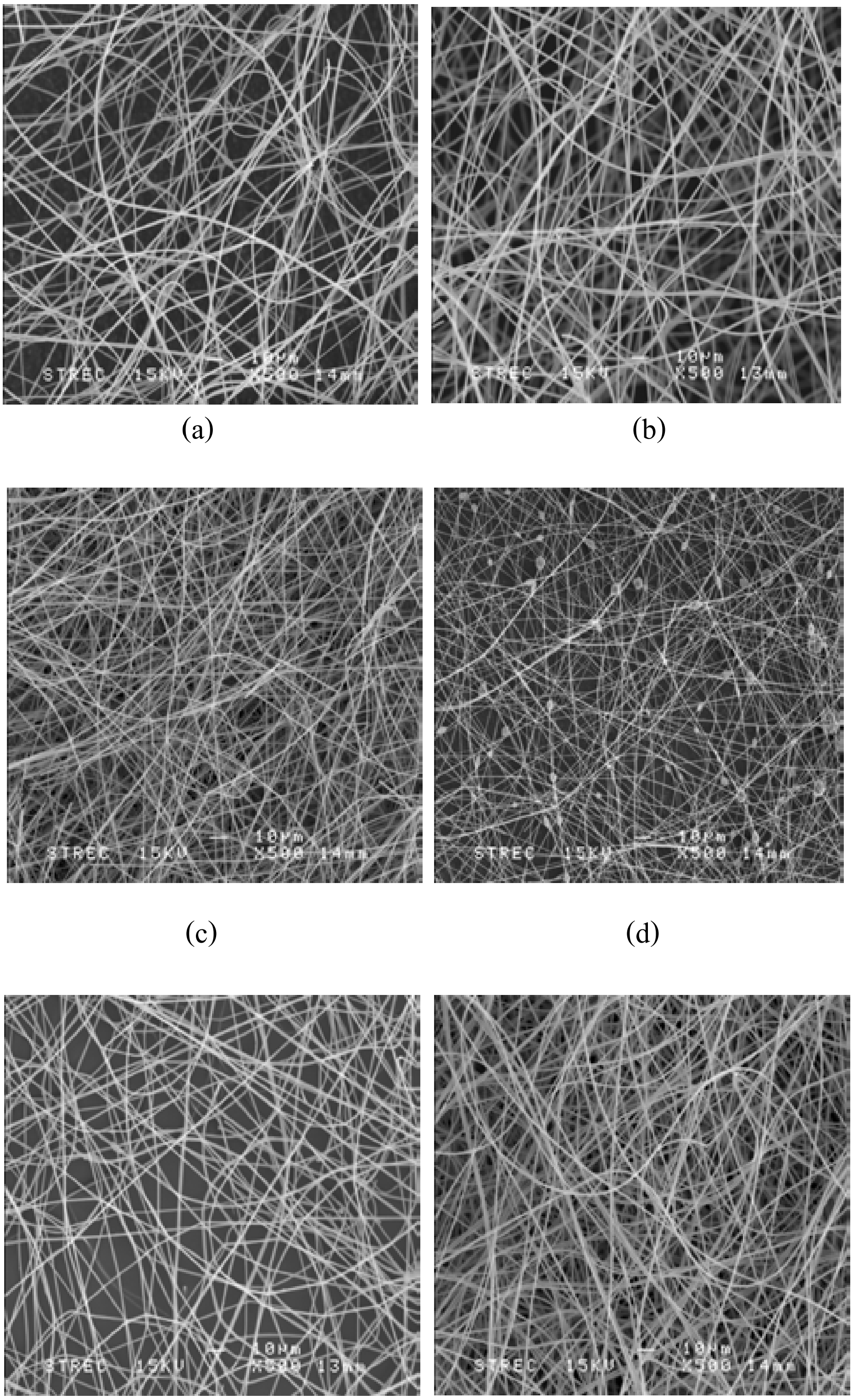
4.3 Effect of process conditions on electrospinning process

The solutions of all three lignin were prepared using 99:1 lignin to PEO ratio at 40 wt% concentration. The voltage was varied between 10 and 20 kV for all solution types. The distance between the needle tip and collector was varied between 10 and 20 cm for CKL system and 10 to 25 cm for WSL and BSL systems.

4.3.1 Morphology of CKL fiber

In CKL system all samples were electrospinnable at all process condition. Figure 4.10 presents SEM images of CKL lignin fiber spun at several process conditions.

From figure 4.10 there are some beads appear in the fiber at low voltage applied (see figure 4.10a and 4.10d) and. The fiber in figure 4.10d was very small comparing to other conditions, as observed at this condition the spinning process was not continuously. This may be caused by there was not enough voltage to initiate a continuously jet. According to figure 4.10b, 4.10 c, 4.10e and 4.10f, the higher voltage applied the better fibers formation. As both the voltage supplied and the resultant electric field have an influence in the stretching and the acceleration of the jet, they will have an influence on the morphology of the fibers obtained [16][17][18]. In this case, a higher voltage will lead to greater stretching of the solution due to the greater columbic forces in the jet as well as the stronger electric field.



(a) (b)

(c) (d)

(e) (f)

Figure 4.10 SEM image of CKL 40% solution electrospun at 15cm 10kV (a), 15cm 15kV (b), 15cm 20kV (c), 20cm 10kV (d), 20cm 15kV (e), 20cm 20kV (f)

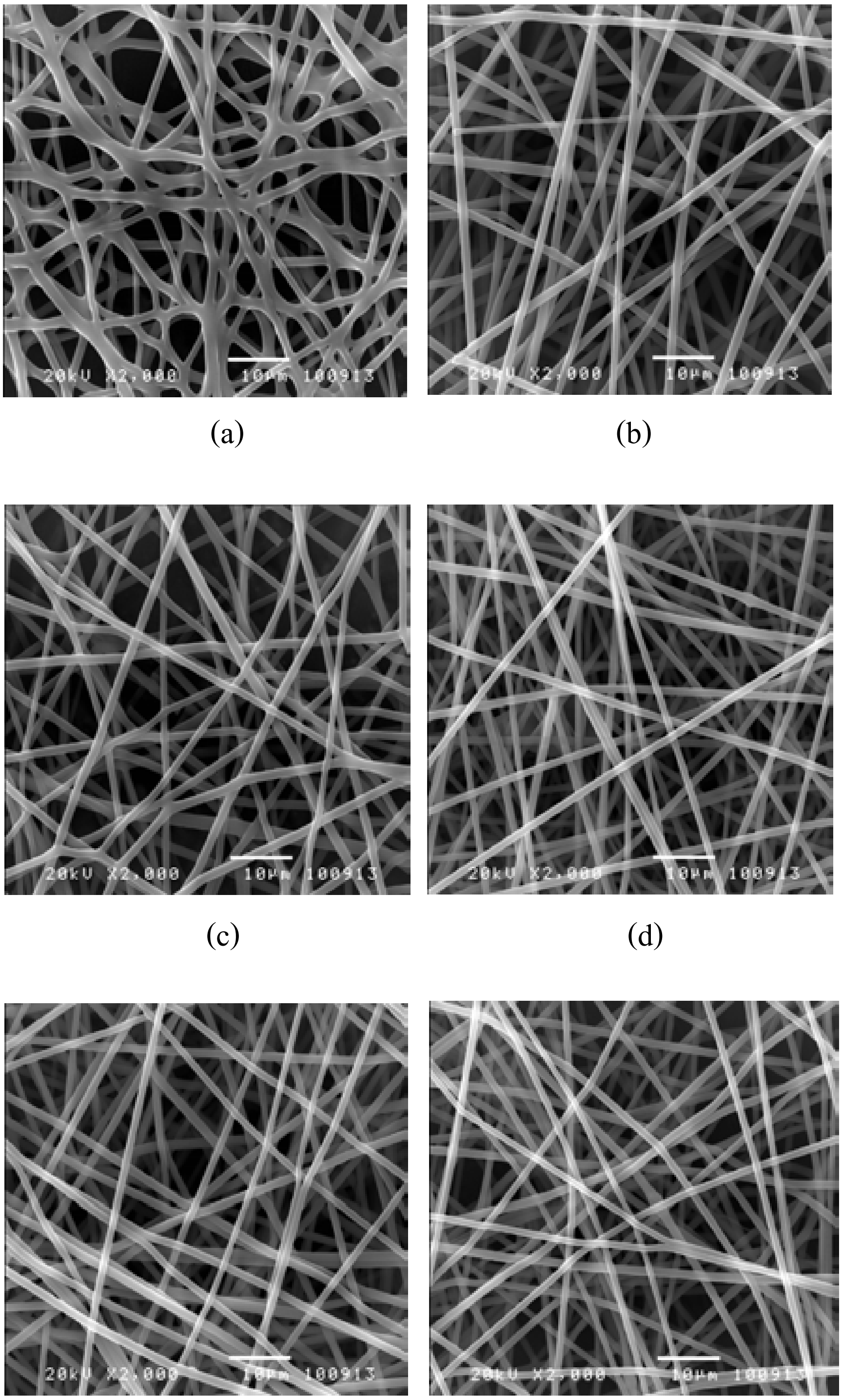
This result was in accordance with the literature reported by Jarusuwannapoom et al. [19]. By given the increased stretching of the jet due to higher voltage, there should be less beads formation.

4.3.2 Morphology of WSL fiber

For WSL system, at the distance of 15cm the fiber was unable to be spun. It was spinnable only at the distance of 20 cm and 25 cm. Figure 4.11 presents SEM images of WSL lignin fibers spun at several process conditions.

For 15 cm distance, there may not have enough time for the solvent to evaporate. The droplet of solution flied to the collector and merged together with other droplets.

At low applied voltage and small distance between tip and collector, figure 4.11a shows the fiber merged together. This may be caused by the reasons discussed earlier. Other process conditions could produce the fiber with uniform morphology.



(a) (b)

(c) (d)

(e) (f)

Figure 4.11 SEM image of WSL 40% solution electrospun at 20cm 10kV (a), 20cm 15kV (b), 20cm 20kV (c), 25cm 10kV (d), 25cm 15kV (e), 25cm 20kV (f)

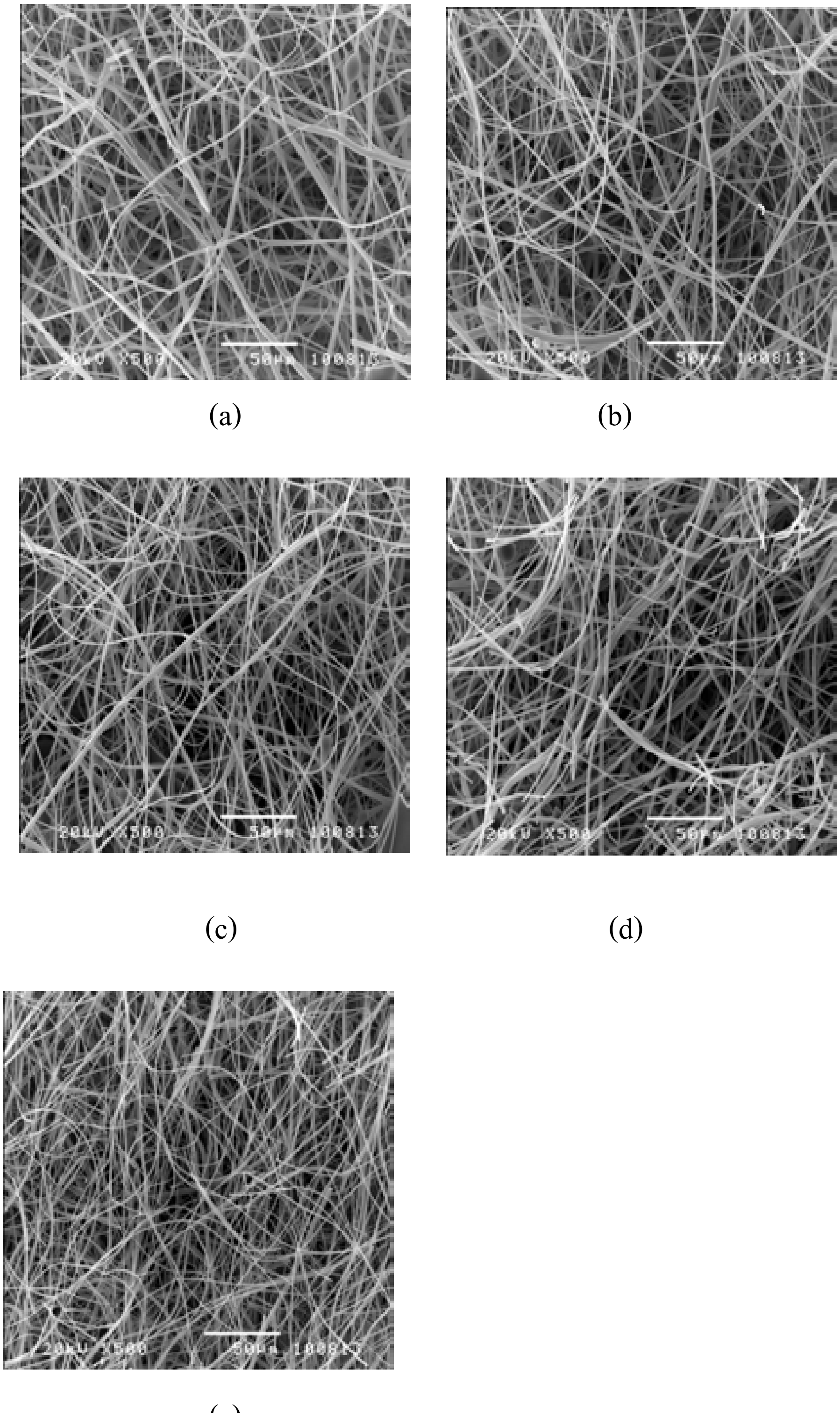
4.3.3 Morphology of BSL fiber

For BSL system, the spinning was worse at the distance of 15cm, where the fiber was unspinnable. At the distance of 20 cm and 25 cm, the fibers were spinnable as shown in Figure 4.12a – 4.12e.

Comparing to CKL and WSL system, the fibers morphology of BSL system is very different. In CKL and WSL system, fibers are smooth and well uniform in size. Unfortunately, in BSL system, the fibers are not uniform and broken into short fibers. Fiber size distribution is varied in wide range of 1.07 – 2.72 micron.

From figure 4.12, some of fibers are broken. Comparing between wood and bark lignin, FTIR results show that wood lignin has more long stretch C-H bond than in the bark. This may cause the continuation of the jet and fiber formation.

As the molecular weight of the polymer represents the length of the polymer chain, then this effect may be caused by the polydispersity of molecular weight of bark lignin. Fang et al. [21] reported that bark lignin of Loblolly pine has polydispersity index higher than stem wood about 50%. High polydispersity index means that the molecular weight of polymer varies in wide range. With much difference in molecular size then the size distribution of the fibers is wide.



(a) (b)

(c) (d)

(e)

Figure 4.12 SEM image of BSL 40% solution electrospun at 20cm 10kV (a), 20cm 15kV (b), 20cm 20kV (c), 25cm 10kV (d), 25cm 20kV (e)

4.3.4 Effect of voltage on diameter of fiber

Figure 4.13 shows the relation between applied voltage and average fiber diameter at the distance between the tip and collector of 15 cm and 20 cm of CKL system. Figure 4.14 and 4.15 show the relation between applied voltage and average fiber diameter at the distance between the tip and collector of 20 cm and 25 cm of WSL system and BSL system respectively.

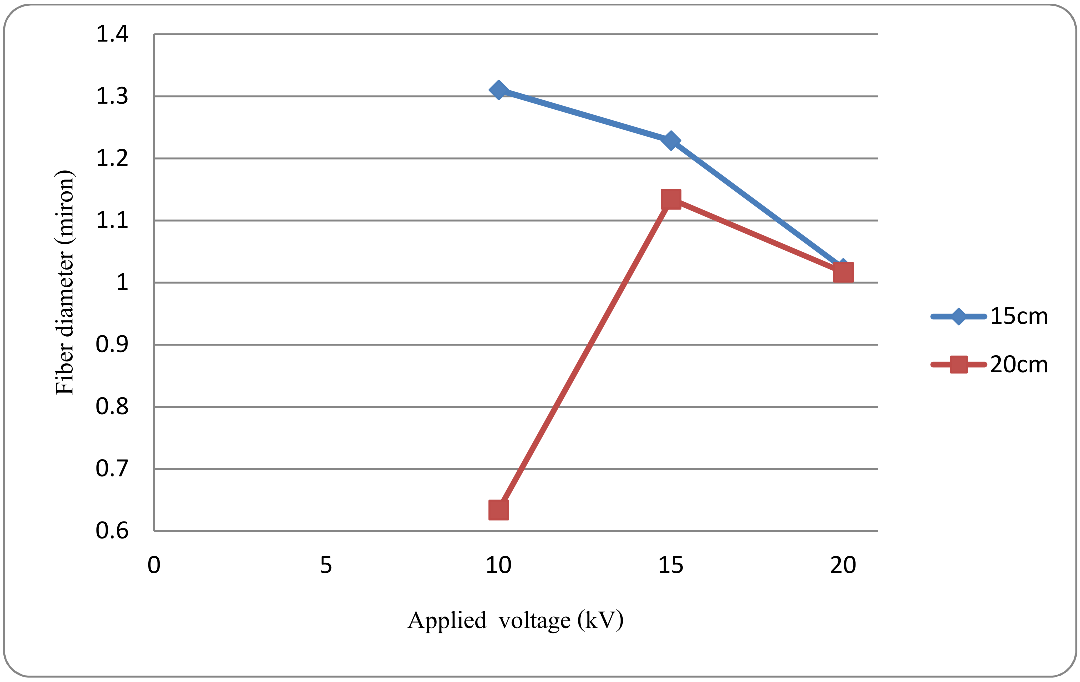


Figure 4.13 relation between applied voltage and average fiber diameter of CKL system

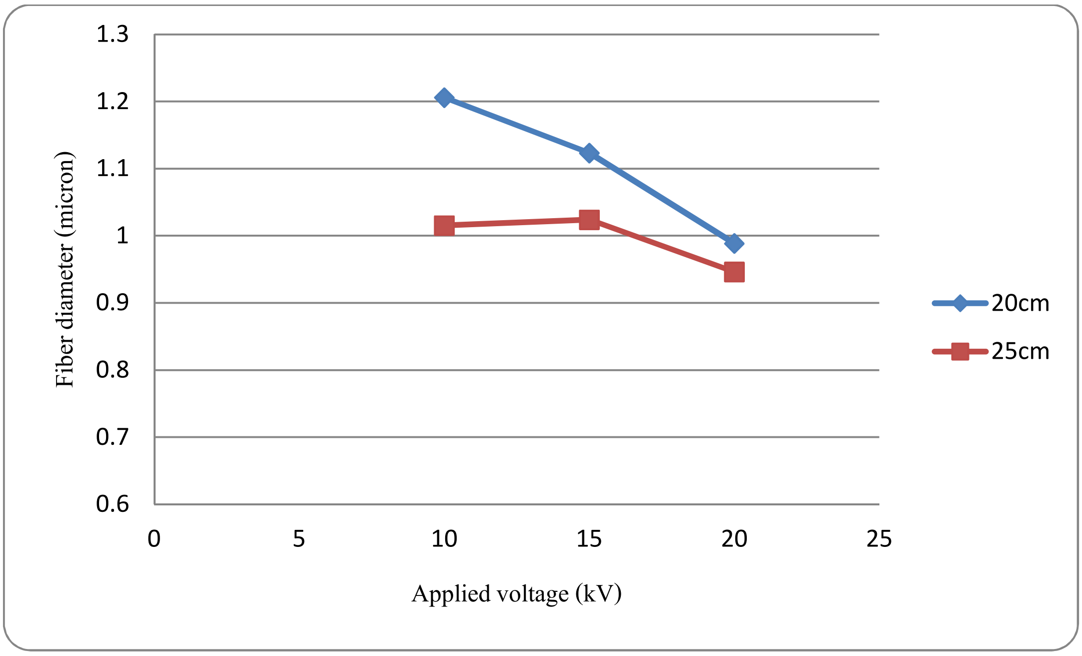


Figure 4.14 Relation between applied voltage and average fiber diameter of WSL system

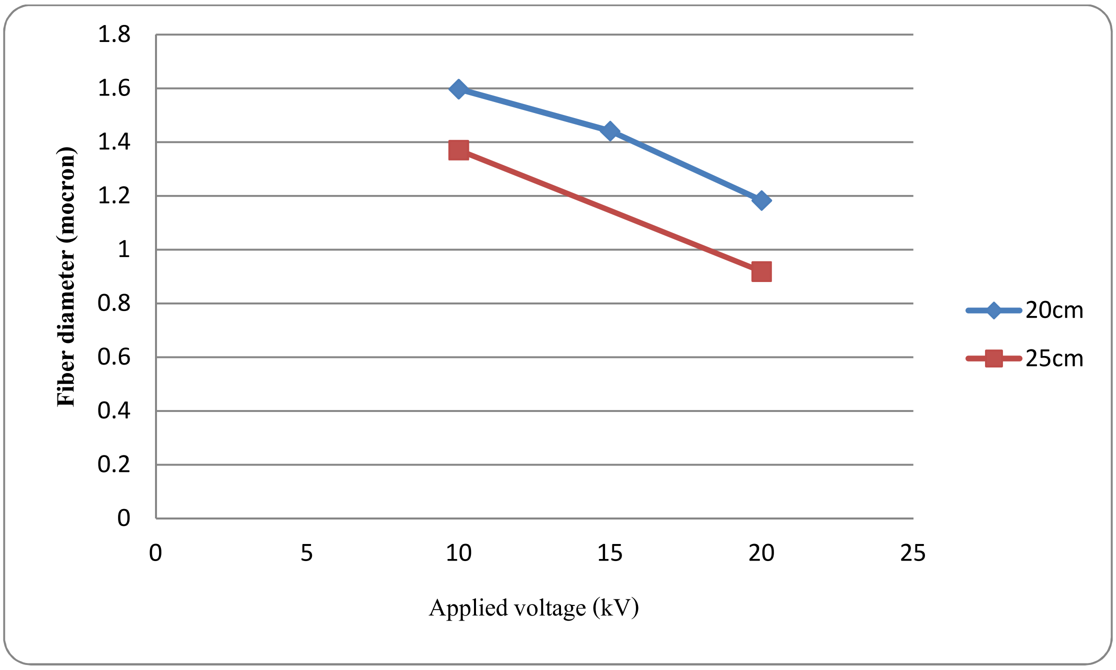


Figure 4.15 Relation between applied voltage and average fiber diameter of BSL system

It was clear for all system that the increased voltage results in decreased fiber diameter. The higher voltage induces higher electrostatic forces on the jet and the higher repulsive forces favor the formation of the thinner fibers [16][18][20][22].

4.3.5 Effect of the distance between tip and collector on diameter

As observed, for CKL system at the distance of 10 cm there was no fiber formation. The droplet of solution flied to the collector and merged together. This is because of there may not have enough time for the solvents to evaporate form the solution before it hits the collector. From figure 4.13, comparing between two system of 15 cm and 20 cm of the distance, the fibers formed at the distance of 20 cm were smaller than that formed at the distance of 15 cm. This may be resulted by longer time for splitting of fiber [17].

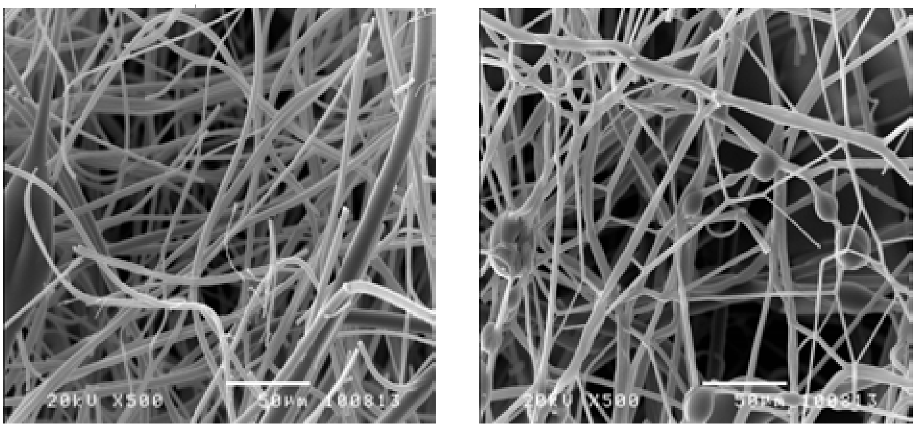
In accordance with CKL system, for WSL and BSL the fibers formed at the distance of 25 cm were smaller than that formed at the distance of 20 cm.

Fiber size is around 1 micron, for nanofiber application which required smaller fiber size to have more surface area. To produce smaller fiber diameter more investigation is required.

4.3.6 Effect of increasing the viscosity

Another way to increase the viscosity of the solution is to increase the polymer concentration. Similar to increasing the molecular weight, an increased in the concentration will result in greater polymer chain entanglements. We have prepared 45wt% with Lignin:PEO ratio is 99:1. The process condition was varied. The distance between the tip and collector was 10 – 25 cm and the applied voltage was 10 – 20 kV.

Unfortunately, the results were not as expected. The viscosity of the solution was too high. The jet could not be formed at low voltage. At 10 cm distance, the jet of the solution merged together when they arrived at the collector. Figure 4.16 shows SEM image of 45% solution electrospun at 20 kv.



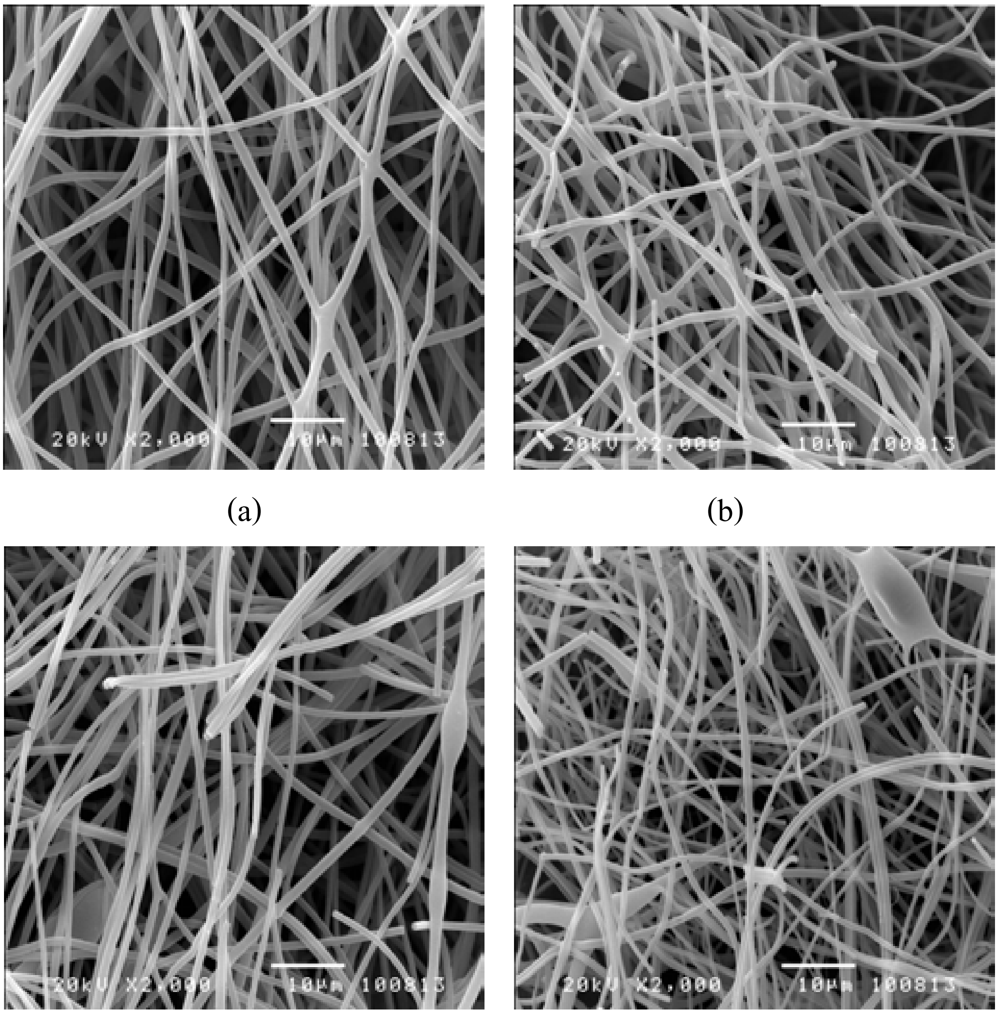
(a) (b)

Figure 4.16 SEM image of BSL 45% solution electrospun at 20cm 20kV (a), 25cm 20kV (b)

From figure 16, comparing to system of 40% solution, the fiber morphology are worse. Fiber sizes are not uniform and beads are found.

4.4 Morphology of carbon fiber

Lignin fiber were stabilized and carbonized according to the procedure described in chapter III. Morphologies of the carbon fiber are shown in figure 4.17**.**



(a) (b)

(c) (d)

Figure 4.17 SEM images of carbon fiber produced from lignin fiber: CKL system 15cm 15 kV (a), 15cm 20 kV (b), BSL system 25cm 10 kV (c), 25cm 20 kV (d)

From figure 4.17, it can be seen that smaller lignin fiber diameter results in fusion of fibers (Figure 4.17 b and 4.17 d). The fusion may be caused by the stabilization process. The heating rate during the stabilization was too high. Reactions occurring during thermostabilization increase glass transition temperature (T_g) of lignin. As increased the temperature at slow heating rate, T_g of lignin could increased faster than the temperature. Then lignin can maintain in glassy state (T_g>T), resulted in non-tacky. At higher heating rate may not be able to maintain T_g>T. Thus the lignin entered in liquid-rubbery state, tacky and fused together.

Hardwood lignin has glass transition temperature about 83°C and PEO has about -57°C. It has been reported that blending Lignin with PEO, decreased T_g of blend polymer [4] which effect the stabilization process.

The carbon fibers diameter was reduced about 20% comparing to its lignin fibers.

CHAPTER V

CONCLUSION

5.1 Conclusion

Carbon fiber could be produced from lignin from several sources. Bark soda lignin has lowest molecular weight compared to commercial Kraft lignin and wood soda lignin which affects the viscosity of solution. Bark lignin is consisted of aromatic skelton in greater extent than that in wood lignin. Due to low viscosity of lignin, none of Lignin/DMF solution at any concentration could be electrospun without adding blending polymer. Only 1% of PEO (Mw = 600,000) could facilitate the fiber formation of lignin solution. At low distance between the tip and the collector, the solution merge together on the collector, this was due to short time for the solvent to evaporate. Increasing applied voltage results in decreased fiber diameter. Fiber morphology of CKL and WSL system were smooth and uniform. In contrast with BSL system, the fibers were not uniform and broken into short pieces. Carbon fibers produced from lignin fibers have a good morphology. Some fibers fusion occurred due to high heating rate of stabilization process. Different blending polymer with higher T_g is required in order to produce carbon fiber from bark lignin.

5.1 Recommendations for future studies

In this study effect of type of lignins and various processing parameters such as the concentration of solution, applied voltage, and working distance were investigated. Some recommendations for future work are listed as follows:

1. Even DMF is good to dissolve lignin, however it has high boiling point (153^{o}C) which is more difficult to evaporate. Lignin solution with lower boiling point solvent should be use to investigate.
2. Quantitative measurement of functional group of lignins should be investigated.
3. Molecular weight of lignins should be investigated.
4. Surface area of carbon fiber should be investigated.
5. Various blending polymers for facilitating the fiber formation should be investigated.

REFFERENCES

[1] U.S. Department of agriculture (1971), "Bark and Its Possible Uses"

[2] JE Holladay, JF Bozell, JF White, DJohnson (2007), "Top Value-Added Chemical from Biomass, Volume 2", U.S. Department of Energy

[3] Xiaosong Huang (2009), "Fabrication and Properties of Carbon Fibers", Materials 2009, 2, 2369 – 2403.

[4] Kadla, J.F.; Kubo, S.; Venditti, R.A.; Gilbert, R.D.; Compere, A.L.; Griffith, W. "Lignin-based Carbon fibers for Composite fiber application". Carbon 2002, 40, 2913–2920.

[5] Kubo, S.; Kadla, J.F. "Lignin-based Carbon fibers: Effect of synthetic polymer blending on fiber properties". J. Polym. Environ. 2005, 13 (2), 97–105.

[6] Moses M.H.; Michael S.; Gregory R.; Michael P.B., "Electrospinning and electrical forced jets. I. Stability theory". Phys Fluids Vol.13 No.8 2001, 2201-2236.

[7] Ian Dallmeyer.; Frank Ko.; John F. Kadla. "Electrospinning of Technical

Lignins for the Production of Fibrous Networks". Journal of wood Chemistry and technology, 30: 315 – 329, 2010

[8] Mozaffar A.K.; Sayed M.A.; Ved P.M., "Eucalyptus Bark Lignin Substituted Phenol Formaldehyde Adhesives: A Study on optimization of Reaction Parameters and Characterization". Journal of Applied Polymer Science 2004, 92, 3514 – 3523.

[9] Abdul A.; Mohini S., "Spectroscopic Studies and Evaluation of Thermorheological Properties of softwood and Hardwood Lignin", Journal of Applied Polymer Science 2011, 10, 956-963.

[10] Ivan B., "Characterization of Natural and Technical Lignins using FTIR Spectroscopy", Lulea University of Technology 2008, 020, 1-41.

[11] Li Jingjing., "Isolation of Lignin from Wood", Saimaa University of Applied Sciences 2011.

[12] Solar R.; Kacik F.; Melcar I., "The comparison of chemical and structural differences of Caribean pine (Pinus caribea L.) wood and bark lignin", Springer-Verlag 1992, 50, 291-294

[13] Solar R.; Kacik F.; "Comparative study of Caribbean pine (Pinus caribaea

L.) wood and bark dioxane lignin", Springer-Verlag 1993, 51, 347-352

[14] John M.F.; Joseph., "Thermal Decomposition of Polystyrene: Eflect of Molecular Weight", Journal of Polymer Science 1974, 12, 217-220

[15] Daojie D.; Arther L.F., "Intrinsic viscosity and the molecular weight of Kraft lignin", Polymer 1995, 36, 2075-2078.

[16] S. Ramakrishna, K. Fujihara, W.-E. Teo, T.-C. Lim, Z. Ma, "An Introduction to Electrospinning and Nanofiber", Toh Tuck Link, Singapore: World Scientific Publishing (2005).

[17] Xiao Y., "Morphology of ultrafine polysulfone fibers prepared by electrospinning", Polymer Int (2004), 53, 1704 – 1710.

[18] Mohamed C.; George S., "Effect of Experimental Parameters on the Morphology of Electrospun Nylon 6 fibres", International Journal of Basic & Applied Sciences, 10, 70-78,

[19] Jarusuwannapoom T, "Effect of solvents on electro-spinnability of polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers", European Polymer Journal 2005, 41, 409-421.

[20] Ayse G.S.; Ali S.A.; Filiz A., “Effect of Voltage on Morphology of Electrospun Nanofibers”, Istanbul Technical University.

[21] Fang H.; Preet M.S.; Arthur J.R., “Characterization of Milled Wood Lignin (MWL) in Loblolly Pine Stem Wood, Residue, and Bark”, Journal of Agricultural and Food Chemistry 2011, 59, 12910–12916.

[22] Lee, J.S., Choi, K.H., Ghim, H.D., Kim, S.S., Chun, D.H., Kim, H.Y. and Lyoo, W.S. Role of molecular weight of atactic poly(vinyl alcohol) (PVA) in thestructure and properties of PVA nanofabric prepared by electrospinning,” , Journal of Appl.Polym. Sci 2004, 93, 1638-1646.

[23] Alexey V.; Andrzej K., “ CHALLENGE IN INDUSTRIAL APPLICATIONS OF TECHNICAL LIGNINS”, BioResources (2011), 6(3), 3547-3568.

[24] H.Janshekarand,; A.Fiechter. “Lignin: Biosynthesis, Application, and Biodegradation”, Dept. of Biotechnology, Swiss Federal Institute of Technology.

[25] Z.-M. Huang, Y.-Z. Zhang, M. Kotaki, S. Ramakrishna, “A review on polymer nano fibers by electrospinning and their applications in nanocomposites”, Comp. Sci. Tech. 63 (2003) 2223.

[26] Otani, S.; Fukuoka, Y.; Igarashi, B.; Sasaki, K. Method for producing Carbonized lignin fiber. US Pat. 3461082, 1969.

[27] Kubo, S.; Uraki, Y.; Sano, Y. Preparation of Carbon fibers from softwood lignin by atmospheric acetic acid pulping. Carbon 1998, 36, 1119–1124.

[28] Kadla, J.F.; Kubo, S.; Venditti, R.A.; Gilbert, R.D.; Compere, A.L.; Griffith, W. "Lignin-based Carbon fibers for Composite fiber application". Carbon 2002, 40, 2913–2920.

[29] Braun, J.L.; Holtman, K.M.; Kadla, J.F. Lignin-based Carbon fibers: Oxidative thermostabilization of kraft lignin. Carbon 2005, 43, 385–394.

[30] Lallave, M.; Bedia, J.; Ruiz-Rosas, R.; Rodr´ıguez-Mirasol, J.; Cordero, T.; Otero, J.C.; Marquez, M.; Barrero, A.; and Loscertales, I.G., "Filled and hollow ˚Carbon nano fibers by Coaxial electrospinning of alcell lignin without binder polymers", Adv. Mater. 2007, 19, 4292–4296.

[31] Seo, D. K.; Jeun, J. P.; Kim, H. B.; Kang, P. H. , "PREPARATION AND CHARACTERIZATION OF THE CARBON NANOFIBER MAT PRODUCED FROM ELECTROSPUN PAN/LIGNIN PRECURSORS BY ELECTRON BEAM IRRADIATION", Adv Mater. Sci, 2011, 28, 31.

[32] Kubo, S.; Kadla, J. F. Hydrogen bonding in lignin: a Fourier transform infrared model compound study. Biomacromolecules 2005, 6, 2815–21.

VITA

Mr.Manit Pulsawad was born on March 6th, 1985 in Nonthaburi province, Thailand. He graduated the Bachelor's degree of engineering with major in Chemical engineering from Chulalongkorn University, Bangkok, Thailand.

LIST OF PUBLICATION

Manit Pulsawad and Varong Pavarajarn. “Production of carbon fibers from eucalyptus bark lignin by electrospinning”. The 29th National Graduate Research Conference (NGRC29), Mae FahLuang University, Thailand, October 24 -25, 2013.