



HOKKAIDO UNIVERSITY

Title	Surface modification of synthetic polymer sheet by direct electrospinning of cellulose acetate
Author(s)	ALI, MD. MOMOTAZ
Degree Grantor	北海道大学
Degree Name	博士(農学)
Dissertation Number	甲第13764号
Issue Date	2019-09-25
DOI	https://doi.org/10.14943/doctoral.k13764
Doc URL	https://hdl.handle.net/2115/75867
Type	doctoral thesis
File Information	Md_Momotaz_Ali.pdf



**Surface modification of synthetic polymer sheet
by direct electrospinning of cellulose acetate**
(セルロースアセテートの直接電界紡糸による合成高
分子シートの表面改質)

Md. Momotaz Ali

Doctoral thesis

Supervisor: Professor Yasumitsu Uraki

Laboratory of Forest Chemistry
Division of Environmental Resources
Graduate school of Agriculture
Hokkaido University, Sapporo, Japan.

September 2019

Contents

Abbreviation list	iii
Chapter 1 General Introduction	1
1.1 Synthetic and bio-based polymers to value-added materials.....	1
1.2 Source and significance of natural (green) polymer	2
1.3 Cellulose and its usefulness.....	5
1.4 Cellulose acetate and its prospect.....	8
1.5 Concept of electrospinning.....	11
1.6 Electrospun fibers deposition substrate	12
1.6.1 Electrospinning on aluminum foil	12
1.6.2: Electrospinning on Polyurethane (PU) sheet.....	12
1.7 Strategy for making polishing material with very smooth surface.....	14
1.8 Research objectives	15
Chapter 2 Optimization of CA concentration and solvent ratio on aluminum foil.....	17
2.1 Introduction	17
2.1.1 Electrospinning.....	17
2.1.2 Utilization of natural bio-polymer	18
2.2 Experimental.....	19
2.2.1 Materials	19
2.2.2 Solubility check of WSCA and CDA in different solvent by electrospinning	20
2.3 CA concentration.....	25
2.3.1 Water soluble cellulose acetate (WSCA)	25
2.3.2 Cellulose diacetate (CDA).....	25
2.4 Characterization.....	26
2.4.1 Solubility check in 100 % organic solvent:	26
2.4.2 Solubility check in different ratio with DMF:	26
2.5 Result and discussion	29
2.5.1 Solubility check of WSCA and CDA in aqueous solvent system in DMF and acetic acid	29
2.5.2 WSCA soluble in 100 % of water and DMF and CDA soluble in 100 % of acetone, acetic acid and DMF.....	31
2.5.3 Different CA concentration and fiber morphology of CAs (WSCA and CDA) with different aqueous solvent system.....	33
Chapter 3 Preparation of CA fiber (WSCA and CDA) on electrically non-conductive Polyurethane (concave-convex) sheet through electrospinning	38

3.1 Introduction	38
3.2 Experimental.....	40
3.2.1 Materials	40
3.2.2 Electrospinning WSCA and CDA polymer solution on PU sheet as a collector.....	41
3.2.3 Electrospun fiber fixation with PU sheet using mixed solvent treatment during spinning	45
3.2.4 Determination of electrospun fiber deposition amount on PU sheet	48
3.2.5 Preparation of regenerated cellulose fiber from CA fiber through saponification	50
3.2.6 Characterization.....	52
3.7 Result and discussion	59
3.7.1 Electrospinning of WSCA on PU sheet with different amount fibers	59
3.7.2 Electrospinning of CDA on PU sheet with different amount fibers	60
3.7.3 Fiber fixation with PU sheet	62
3.7.4 Regenerated cellulose fiber from CAs (WSCA and CDA) characterized through FTIR spectra by saponification.	62
3.7.5 Regenerated cellulose fiber from CAs (WSCA and CDA) characterized	66
through X-ray diffraction pattern by saponification.....	66
Chapter 4 Evaluation of surface change of non-saponified and saponified electrospun fibers coated PU sheet through Tribology measurement	68
4.1 Introduction	68
4.2 Experimental.....	69
4.2.1 Materials	69
4.2.2 Sample preparation for friction coefficient measurement using Tribogear instrument.	70
4.2.3 Processing of tribological raw data	70
4.3 Result and discussion	71
4.3.1 Friction coefficient measurement over WSCA and CDA fiber deposited PU sheet	71
Chapter 5 General conclusion	79
Reference.....	81
Acknowledgement.....	90

Abbreviation list

CAs	:	Cellulose acetate (s)
WSCA	:	Water Soluble Cellulose Acetate
CDA	:	Cellulose diacetate
PU sheet	:	Polyurethane sheet
PET	:	Poly(ethylene terephthalate)
EtOH	:	Ethanol
DMF	:	Dimethylformamide
NMMO	:	N-methylmorpholine
DMSO	:	Dimethylsulfoxide
AMIMCl	:	1-allyl-3-methylimidazolium chloride
ES	:	Electrospinning
i. d.	:	Inner Diameter
kV	:	Kilo Volt
ARH	:	Air Relative Humidity
DS	:	Degree of Substitution
Cellulose I and II	:	Cellulose I and Cellulose II
CNF	:	Cellulose nanofiber
CD	:	Compact Disk
HD	:	Hard Disk
3D	:	3-Dimensional Microscope
SEM	:	Scanning Electron Microscope
ATR	:	Attenuated Total Reflection
FTIR	:	Fourier Transform Infra-Red
XRD	:	X-ray diffraction

Chapter 1 General Introduction

1.1 Synthetic and bio-based polymers to value-added materials

Generation of new technologies by utilizing natural resources both renewable and non-renewable is an important subject owing to the natural abundance and renewability of the raw materials ([Santos, et al., 2018](#)). Fabrication of polymeric materials using these resources, based on new and innovative technologies can increase the widespread utilization of natural resources for the society. Thus, polymeric product development using innovative technologies is an urgent requirement. There are two types of polymers obtained from the nature such as fossil resources and bio-based resources. Fossil resource-based polymers include oil, coal, and natural gas and bio-based polymers include cellulose, starch, silk, chitin, protein, DNA etc. Generally, fossil resource-based polymer is not renewable over time, whereas bio-based polymer is renewable within human scale span. From the time line of synthetic polymer invention, it has been used in multiple aspects of human demand. Now-a-days, the application of synthetic polymers are almost everywhere and it is about 99% of the total plastic production that comes from fossil resources ([Abdul Latif, et al., 2019](#); [Lenart, et al., 2016](#)). The limited fossil resources are depleted day by day for such massive consumption ([Capellán-Pérez, et al., 2014](#); [Hottle, et al., 2013](#)). Thus, the abundant natural plant-based biomasses are the best alternatives to reduce the dependency on fossil resources. This can eventually optimize the utilization of natural and synthetic polymers for sustainable and new technology-oriented biosynthetic product manufacturing ([Marques, et al., 2018](#)). On the other hand, combine utilization of natural and synthetic polymers can reduce extra pressure on the petroleum resources

to some extent and at the same time it might accelerate the utilization of natural polymer.

In 2013, 299 million tons of petroleum-based polymers were produced from fossil resources (Shaghaleh, *et al.*, 2018). Non-renewable average energy consumption rate is increasing day by day approximately 4% in each year (Shaghaleh, *et al.*, 2018). In another report, it was revealed that about 200 million tons of conventional plastics are derived from petroleum-based resources in each year (Gironi and Piemonte, 2011). Thus, the price of petroleum-based raw materials has increased over the time and depleted the fossil resources that cannot be recovered, whereas the demand is increasing exponentially. Utilization of fossil resources in synthesis process of synthetic polymers releases some toxic substances CO₂, CO, SO₂, and N₂O, which are also known as greenhouse gases, in the environment and contribute to increasing the global warming, and acid rain, which might be minimized using bio-based natural resources. Whereas, public health and the safety risks would be reduced in near future due to the exponentially increasing utilization of natural (green) resources for energy consumption. These indicate that the lignocellulosic biomass would be the best alternative feedstock from natural resources for plastic production with proper technology development (Al-Battashi *et al.*, 2019). Therefore, fabrication of bio-based materials using renewable and abundant resources is the main target of my research.

1.2 Source and significance of natural (green) polymer

Natural polymers are obtained from two sources such as biomass and phytomass. Biomass is the total weight of living organism, while phytomass is the total weight of plant biomass. Massive amount of biomass is produced (about 180 billion tones) all

over the world in every year (Festucci-Buselli, *et al.*, 2007). Recently, woody biomass from natural resources such as cellulose, hemicellulose and lignin, among which cellulose and lignin are frequently used for advanced technology generation due to existent of its availability and bio-friendly properties in nature. This huge amount of natural polymer is produced through photosynthesis process in each year (Lewandowski, 2013). Photosynthesis is the process to convert CO₂ and water into Sugar (carbon compounds) and Oxyzen by the living plant cells using sunlight, only energy source on earth from sun as shown in [Figure 1-1].

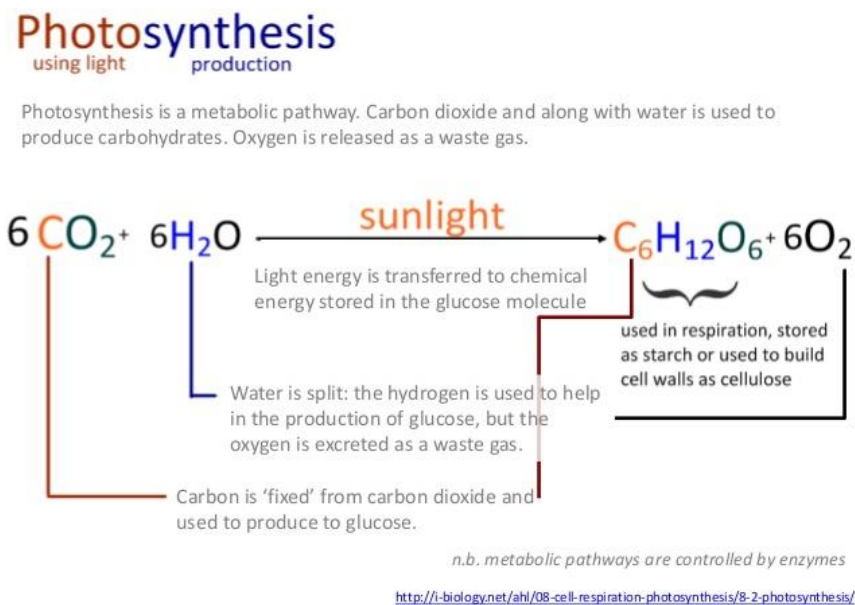


Figure 1-1. General photosynthesis pathway.

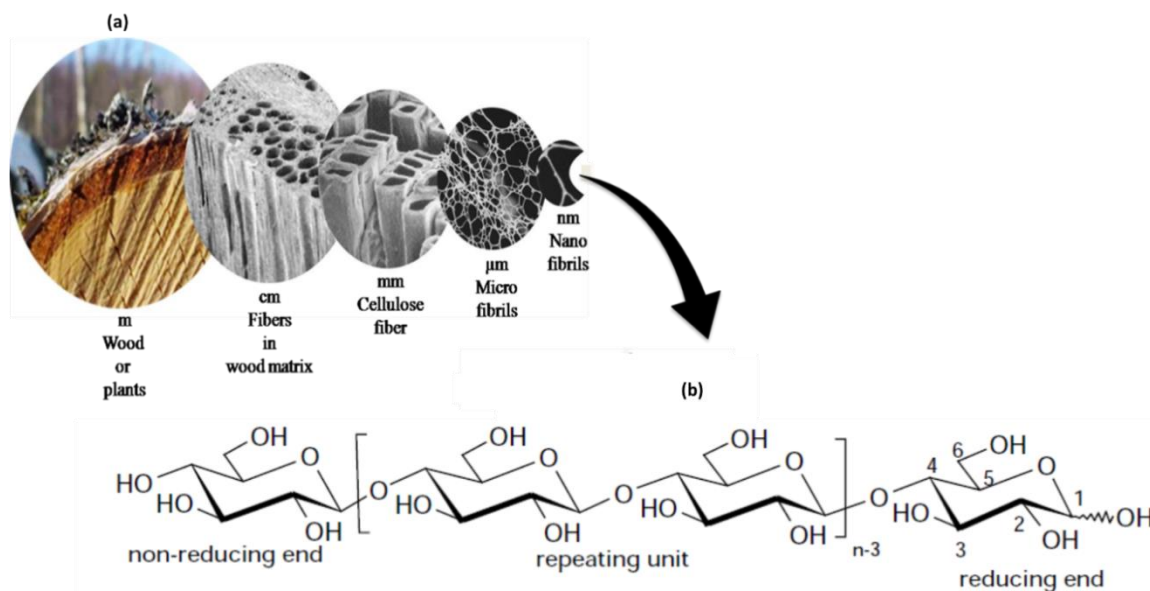
During photosynthesis, **green polymer** is produced in the plant cell walls where alpha glucose produced amylose (starch) and beta glucose is responsible for cellulose production. Normally, cellulose (beta glucose) is not digested in human stomach. After utilizing in the intended purposes, the remain part is abundant biomass such as agricultural waste (straw of rice, wheat, sugarcane bagasse, corn stover, etc). Sometime, these waste materials are decomposed by some microorganism to increase

soil fertility. On the other hand, woody perennial tree timber is used for construction purposes, after its intended utilization, rest of the part is woody biomass. Woody biomasses are frequently used as fuel purposes for cooking. However, after the intended use, rest of the part is abundant resources from annual plants and perennial trees. Furthermore, these abundant resources are not competed with food to human consumption, which is mostly consisting of green polymer. Green or biodegradable polymers are special type of polymer, which is broken down after its intended utilizations; the decomposition process is proceeded through microbial degradation by bacteria and fungi. The yields of microbial activity, natural products such as gases (CO_2 and N_2), water, humus and inorganic salt are released in the soil.

From the viewpoint of green polymer utilization, no harmful products are released in the environment. Huge amount of biomass contains green polymer, which can be produced with in a short time (half yearly or annually) in every season such as agricultural crop production span. In the same manner, perennial herb, shrub and trees also have been produced huge amount of green polymer in each year. After its intended utilization, most of the parts are abundant from seasonal and perennial plants in the nature. This abundant plant part consists of cellulose (35 - 50 %), hemicellulose (25 - 35 %) and lignin (15 - 35 %) depending on basis of the plant species. That's why, renewable resources are abundant and available in nature. In woody biomass, cellulose is the major component in the plant cell walls. Therefore, green polymer-based materials preparation from renewable feedstock has drawn much attention. For the sustainable production processes based on renewable woody biomass, cellulose utilization is one of the key factors to use in bio-based materials preparation.

1.3 Cellulose and its usefulness

Cellulose is a linear polysaccharide. It consists of β (1 $\rightarrow$ 4) anhydro-D-glucopyranose (cellobiose) units as shown in [Figure 1-2 (b)].



Figureure. 3-1. Schematic hierarchical structure of wood fiber (a) and Molecular structure of cellobiose repeated unit for cellulose (b) (Sixta, 2006).

It is the most abundant lignocellulosic organic compound with complex (supramolecular) structure in the plant (Wang, *et al.*, 2015). It has different polymorphism properties. Polymorphism is the ability of a solid material to exist in more than one form or crystal structure. There are four different types of cellulose polymorph (I, II, III_I and IV_I) based on unit cell exists in cellulose chemistry (Gong, *et al.*, 2017). It can be found as the crystal and amorphous structure in the natural polymer. In the cellulose science, cellulose I and II are the form mostly reported and investigated (Wang, *et al.*, 2014). It is also reported that, cellulose I is easily converted into cellulose II through mercerization and alkali treatment process, but it is not reversible (Sarko and Muggilb, 1973; Diddens, *et al.*, 2008; Marchenko, 1984; Kolpak

and Blackwell, 1976). Molecular structure of cellulose I and II as shown in [Figure 1-3].

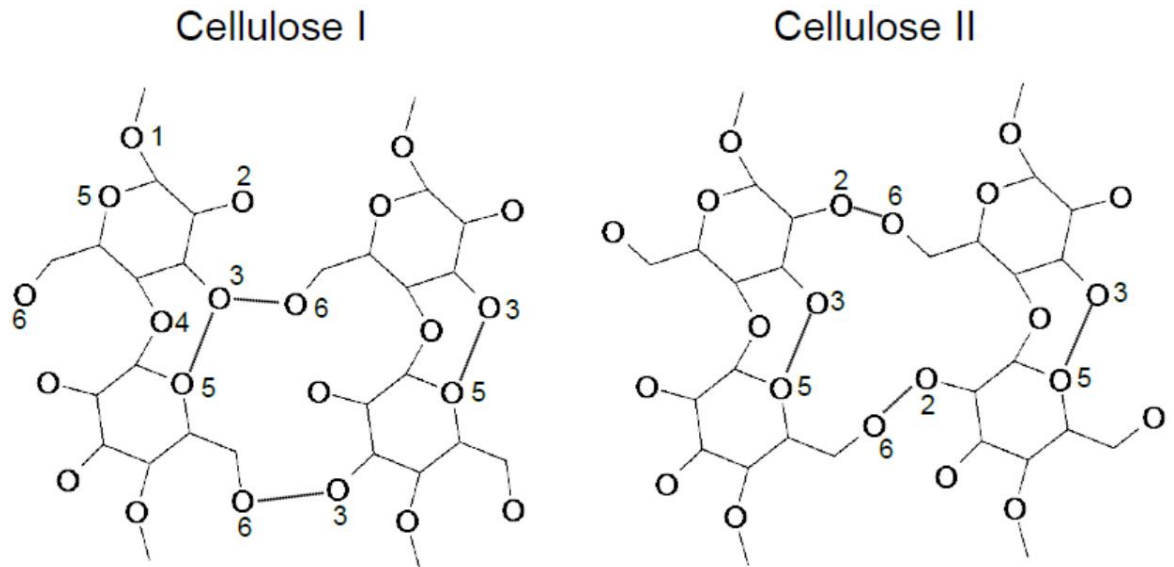


Figure 1-3. Hydrogen bonding pattern of cellulose I and cellulose II.

Crystal structure of cellulose depends on their orientation and within their respective unit cells (Nishiyama *et al.*, 2003). Unit cell is the most basic and smallest repeating structure of any solid. Native celluloses consist two crystal forms of allomorph (I_α and I_β) (Eichhorn and Davies, 2006) [Figure 1-4].

→ I_α is dominant in, e.g.,
bacterial cellulose and algae

→ I_β is dominant in higher plants
(e.g. wood, cotton)

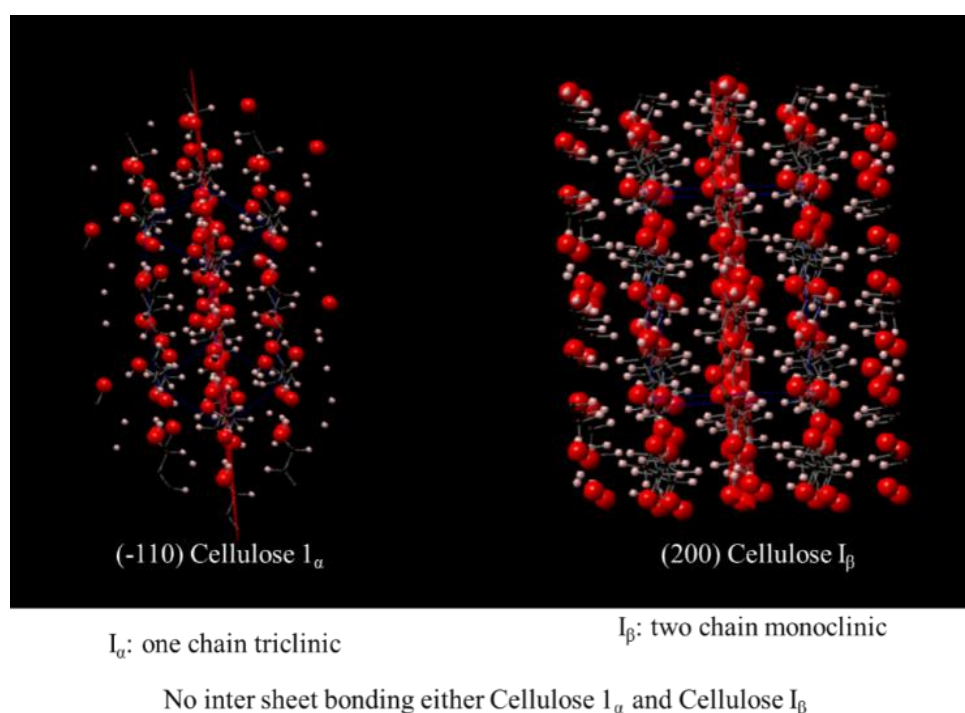


Figure 1-4. Structural differences: cellulose I_{α} and cellulose I_{β} .

Allomorph is the form of different crystalline structure in same chemical compound. Cellulose I_{α} has a triclinic one-chain unit cell, with Van Der Waals interactions where cellulose chain stacks in parallel fashion. Cellulose I_{β} has a monoclinic two-chain unit cell, where cellulose chain stacks in anti-parallel fashion. Cellulose III_I is obtained from cellulose I by liquid ammonia or various amines treatment process. Cellulose IV_I could be prepared by glycerol treatment at 260 °C after transformation into cellulose II or III (Wada, *et al.*, 2004). Cellulose I cannot be directly transformed into cellulose IV due to its high crystallinity. Cellulose II is little weaker than cellulose I, due to crystalline polymorph of cellulose. It has many attractive properties such as high specific elastic modulus property (mechanical) than steel (Nogi, *et al.*, 2009), light weight than iron (Carrick and Larsson, 2014), thermal stability (Liu *et al.*, 2017; Wang *et al.*, 2014), specific high surface area (Sehaqui, *et al.*, 2011). Elastic modulus of the crystalline region of cellulose I is reported around 135

GPa (Sakurada, *et al.*, 1962; Nishino, *et al.*, 1995). Elastic modulus of regenerated cellulose is around 110 GPa from X-ray diffraction analysis (Matsuo, Sawatari, Iwai, & Ozaki, 1990) and 160 GPa from theoretical estimation (Tashiro and Kobayashi, 1991), which is also much higher than conventional synthetic polymer like plastics (Sakurada and Nakama, 1964). Moreover, regenerated cellulose is very similar to that of natural cellulose. Thus, it can be used as a reinforcing agent (Sakakibara, *et al.*, 2017); (Chupin *et al.*, 2017; Lukanina *et al.*, 2018; Cazón, *et al.*, 2018) or filler to improve the mechanical property of plastics. Thus, owing to these exclusive properties, cellulosic materials collected much attention to conversion into value added functional materials available from abundant resources.

1.4 Cellulose acetate and its prospect

Generally, natural cellulose is combined with hemicellulose and lignin in the plant cell walls. Lignin cannot be dissolved in water and organic solvents. Therefore, wood component (cellulose, hemicellulose and lignin) isolation is very important. Cellulose can be isolated from woody biomass by pulping and bleaching as shown in [Figure 1-5].

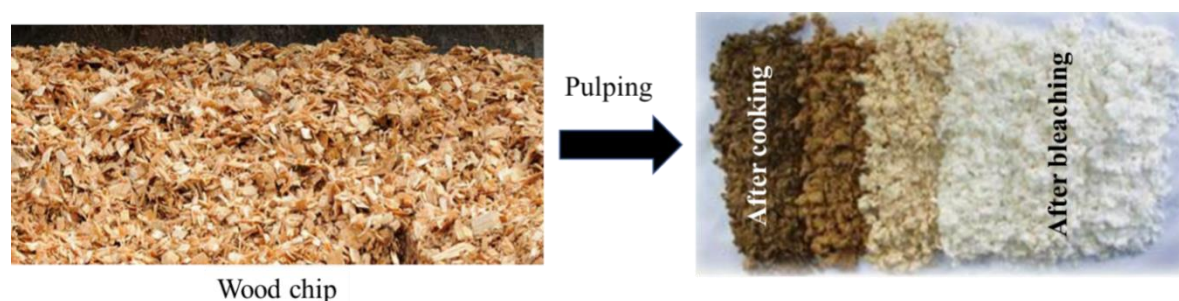


Figure 1-5. Cellulose from wood biomass through pulping and bleaching

This isolated purified cellulose also has solubility problem, which is not easily dissolved in water and many organic solvents. This is because cellulose has complex hydrogen bonding structure with hydrophobic behavior. Hydrogen bonding of cellulose is shown in [Figure 1-6].

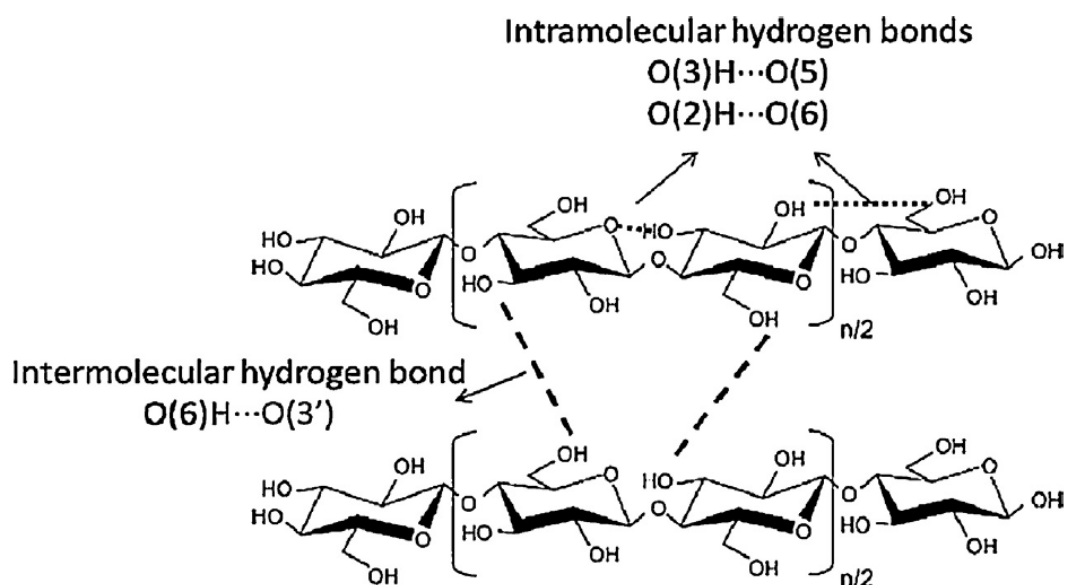


Figure 1-6. Inter and intra molecular hydrogen bonding of cellulose molecule

(Wang *et al.*, 2015).

The hydrogen bonding of cellulose sometime is not accessible by microorganism and fungi, this is because of its hydrolysis process is protected due to its stability and crystallinity. Cellulose is soluble in some typical solvents, but the solvents are expensive and environmentally harmful. Thus, the poor miscibility of cellulose in different solvent is the main constrain, even though it has good flexibility, linearity, mechanical strength, and nontoxic properties. Bio-based polymeric materials preparation from green polymer cellulose with unique morphology and solubility is crucial. Once, it can be miscible in water and organic solvents, unique morphology-

oriented materials would be obtained. Cellulose acetate (CA) is one of the modified cellulose derivatives, which is prepared from natural purified cellulose through acetylation process. This modified cellulose derivatives or natural plastics are soluble in many organic solvents and sometimes in water to make polymer solution for spinning. Electrostatic fiber formation with unique morphology is possible using suitable organic solvent ratio. Therefore, CA is the promising option for fine fiber preparation through electrospinning. Acetylation of cellulose is shown in [Figure 1-7].

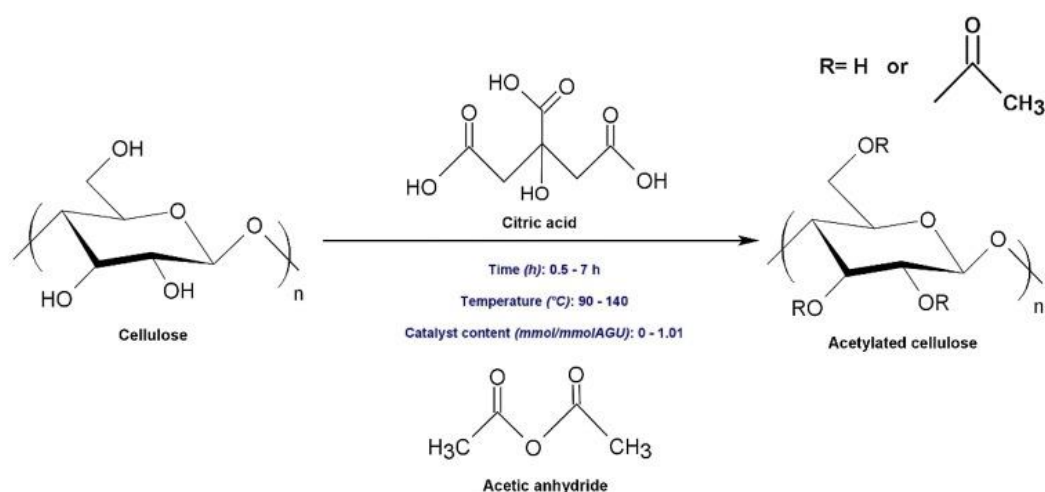


Figure 1-7. Acetylation of cellulose catalyzed by citric acid (Ávila RTamírez, *et al.*, 2016).

Natural fiber preparation from native cellulose is difficult because residual effect of some organic solvent cannot be completely removed from the fiber, yet many researches has investigated the process. However, the residual effect could be removed from the acetylated cellulose fiber upon saponification process. This also advocates that the CA is a promising option for fine fiber preparation applying the electrospinning process.

1.5 Concept of electrospinning

Electrospinning is a promising method to produce nanofiber from wide variety of polymer, because electrospun fiber can be functionalized by simple changes in the process parameters (Zheng, *et al.*, 2007). A concept of electrospinning is very old. The patent of electrospinning concept including fundamental apparatus was firstly released in 1902's (Cooley, 1902). The patents for dry- and melt-electrospinning were released in 1934's (Formhals, 1934) and 1936's (Norton and Mass, 1936) respectively. The electrospinning process has still a central attention because the process can provide micro or nanofibers. To initiate the process, high electrical voltage is applied on polymer solution. The charged polymer solution is formed in Taylor cone shape and the electrical force overcome the surface tension of polymer solution. Liquid jet is ejected from the cone tip to the corrector plate. During flying the solvent is evaporated (Hou *et al.*, 2012; Bhardwaj and Kundu, 2010). The polymeric molecules are elongated and oriented by electrical force (Song *et al.*, 2018; Kongkhlang, *et al.*, 2008). As a result, fine fiber is obtained. Conventional electrospinning setup is shown in [Figure 1-8].

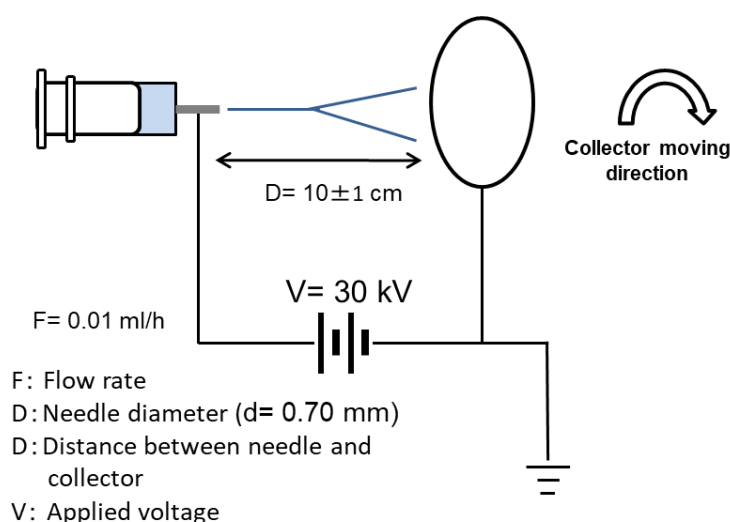


Figure 1-8. Schematic diagram of electrospinning set up to obtain random microfibers

Electrospun fibers have a larger specific surface area (Sehaqui *et al.*, 2011) compared to conventional fiber. It can be applied to wide variety of polymer, including synthetic and bio-based polymer. The obtained nano fibers have various application in multiple fields such as medical application (Cremar *et al.*, 2018; Lukanina *et al.*, 2018; Pourali, *et al.*, 2018; Adepu *et al.*, 2017), filter (D'Halluin *et al.*, 2017), electrode material (Wang and Wallace, 2015), (Liu *et al.*, 2015), advanced composites (Wang *et al.*, 201; Kim, *et al.*, 2015), separation membrane (Arslan, *et al.*, 2016) and sensor (Ding, *et al.*, 2010) etc.

1.6 Electrospun fibers deposition substrate

1.6.1 Electrospinning on aluminum foil

Generally, all most all electrospun fibers are prepared on aluminum foil as a collector substrate material. Because, charged electrospun fibers could be easily deposited on aluminum foil. This is because the surface of aluminum foil is electrically conductive. Therefore, voltage difference can be created between needle tip to grounded collector easily. As a result, charged fibers can be deposited on the conductive collector. Finally, it is easy to collect electrospun fiber from aluminum foil.

1.6.2: Electrospinning on Polyurethane (PU) sheet

Polyurethane (PU) sheet has electrically non-conductive synthetic surface. There are few reports of electrospun fibers prepared on synthetic polymer. As we know, all electrospun fibers are prepared on porous synthetic polymer such as nylon mesh, lyocell mat, glassine paper etc. as a collector substrate (Nicosia *et al.*, 2016; Kakunuri, *et al.*, 2017). All of those substrate materials (synthetic surface) are porous. Therefore, charged fibers are tried to deposit on conductive surface. Before that, the fibers were

attached on the synthetic surface such as nylon mesh (Nicosia et al., 2016). As a result, electrospinning process is successful on synthetic surface. However, to the best of our knowledge there is no report about electrospun fiber on non-conductive surface (non-porous plastic sheet) as a collector material. This is because voltage difference cannot be created between needle tip and collector and the electrical charge is accumulated on plastic surface (non-conductive). Therefore, electrospinning become unsuccessful. As an example, [Mares \(2018\)](#) succeeded electrospinning process on non-conductive surface by hot-melt adhesive process with softening temperature but this is not on synthetic surface.

Additionally, there is no literature report on fiber fixation using a mixture of organic solvent. This is because it is very difficult to keep the fiber morphology and fixation at the same time. That's why non-conductive and non-porous synthetic polymer with concave and convex structure (PU sheet) lamination is the main subject using bio-based polymer through electrospinning. The polyurethane sheet (concave and convex) morphology as shown in **[Figure 1-9]**.

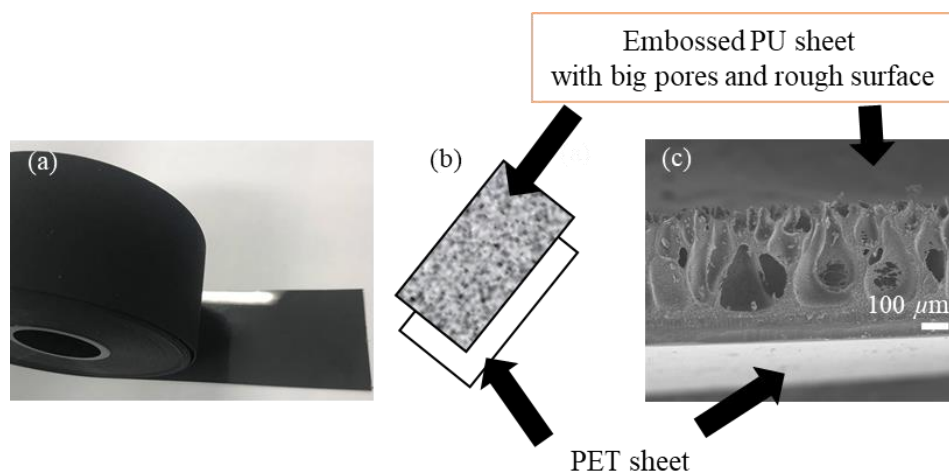


Figure 1-9. Appearance of PU sheet (a), hand writing image of PU sheet structure (b), and cross section (c).

The porous polyurethane sheets are produced as a polishing material for making the compact disk (CD) and hard disk (HD) by Fujibo Company Ltd, Japan (Budinger, 1990; Ho, *et al.*, 2016).

1.7 Strategy for making polishing material with very smooth surface

To prepare polishing material with small pore surface, big pores are changed to small pores by coating with microfibers. Cellulose microfiber is suitable because it has high Young's modulus, low thermal expansion and light weight properties. Cellulose nanofiber (CNF) is more promising because vacant space of pores is fulfilled or occupied with them to make very smaller pores. Therefore, direct coating of CNF seems to be easy and simple method. However, its application is very difficult because general CNF is stored as a diluted suspension (1%), which looks almost gel or hydrogel (Abe and Yano, 2012). There are two possible methods proposed; solution coating and direct deposition of solid material for the surface modification of plastics with cellulose. Solution coating method may not bring high mechanical strength to the surface of plastics, because the regenerated material like film from the solutions normally amorphous and shows low elastic modulus. In contrast, direct deposition method using solid materials, such as fiber, would probably add high elasticity to the surface, because the deposited material, for example CNF, keeps high crystallinity and elastic modulus by this method. Spraying the gel or coating the gel on the plastics will deposit CNF more successfully. However, spraying machine for viscous hydrogel is not popular. Water evaporation will be a bottleneck in the coating method because it takes a long time (Kose, *et al.*, 2011). Thus, electrospinning seems to be a promising alternative method for deposition of solid cellulosic materials (fibers).

Therefore, I propose an alternative method to the CNF direct coating. The polishing material is coated with cellulose acetate (CA) nanofibers, and then CA nanofibers are saponified to regenerate cellulose nanofibers. The reason why CA is used in this nanofiber's preparation is because CA easily dissolves in many organic solvents to make a polymer solution for electrospinning. The CA nanofibers are easy to be made by electrospinning. In order to make the polishing material, I focused on direct electrospinning of CA solutions on the polishing material (PU sheet).

1.8 Research objectives

The aims of this study were

- to prepare electrospun CA fiber from Water Soluble Cellulose Acetate (WSCA) and Cellulose Diacetate (CDA)
- to optimize the organic solvent and CA concentration
- Preparation of electrospun fiber and fiber amount on PU sheet
- to determine the fiber fixation process on PU sheet
- to evaluate the surface roughness change properties through tribology measurement test ([Schön, 2004](#)).

Main objective

Main objective of this study is to change the surface property of non-mesh and non-conductive synthetic polymer (PU) sheet (concave-convex) by laminating with thin CA fibers mat through direct electrospinning of cellulose derivatives.

To achieve above-mentioned objectives, the following schematic plan was prepared as shown in **[Figure 1-10]**.

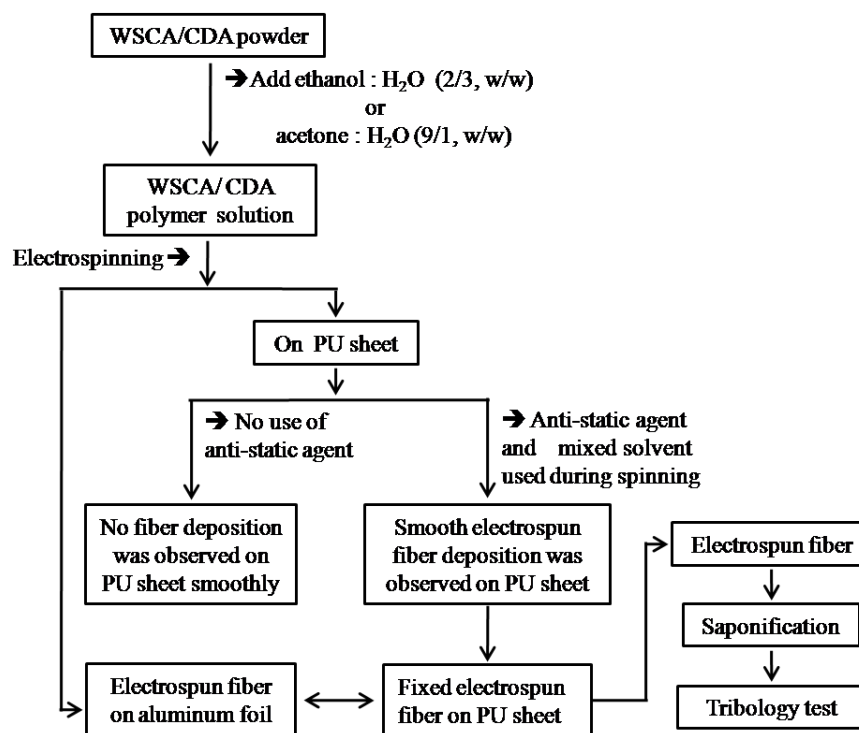


Figure 1-10. Schematic diagram of electrospun microfiber preparation through electrospinning

To achieve the objectives, electrospinning method was chosen for submicron fibers preparation. Two kinds of CAs, cellulose diacetate (CDA) and water-soluble cellulose acetate (WSCA) were used as raw material. CDA is soluble in acetone, a volatile organic solvent, and WSCA was produced as a research sample by Daicel Company (Osaka, Japan) by employing non-toxic solvent water. Furthermore, CAs are easily converted to regenerated cellulose by saponification.

So, fine fibers are easily expected from CAs (WSCA and CDA) through electrospinning with those volatile organic solvent systems. These results are detailed described in **Chapter 2**.

Chapter 2 Optimization of CA concentration and solvent ratio on aluminum foil

2.1 Introduction

2.1.1 Electrospinning

Electrospinning is a very old technique, its concept including a fundamental apparatus was patented at the beginning of 20th century [Cooley, 1902](#). Based on polymer dopes, it is classified into two types, namely polymer melt and polymer solution, which are termed as melt-electrospinning and solution-electrospinning, respectively. Solution electrospinning is further classified into dry electrospinning and wet-electrospinning. In melt-electrospinning, high electric force is applied to the polymer melt at a high temperature to form a jet. The jet coagulates in cold air to produce fibers. In dry-electrospinning, a high electric voltage is applied to a polymer solution. When the electric force exceeds the surface tension of the polymer solution, the charged polymer solution moves as a jet from a nozzle to a collector, and this electrospinning is accompanied by the evaporation of the solvent ([Bhardwaj and Kundu, 2010](#); [Taylor, G. 1969](#)). During the movement, the polymer molecules are elongated and orientated by the electric force. Thus, fibers are formed and occasionally crystallized ([Zheng, et al., 2007](#); [Kongkhlang, et al., 2008](#)). In wet-electrospinning, polymer in the solution is also elongated by the electric force and regenerated fibers are obtained in a coagulation bath with a non-solvent ([Frey, M.W., 2008](#)).

In general, having small fiber diameter ranging from 2 nm to several micrometers is produced by electrospinning process ([Lyons, et al., 2004](#)). Therefore, the electrospun fiber shows a very large specific surface area ([Hardick, et al., 2013](#); [Zhou, et al., 2011](#)) as compared to that of fibers (10 to 500 μm in diameter) produced by conventional spinning processes ([Huang, et al., 2003](#); [Rutledge and Fridrikh, 2007](#)). The thin fibers can be used as scaffolds

tissue engineering (Li, W. J. *et al.*, 2002; Vaz, *et al.*, 2005);(Wan Ju Li *et al.*, 2005; Kwon, *et al.*, 2017; Lukanina *et al.*, 2018) protective cloths to spoilage pathogenic microorganisms (Amna, *et al.*, 2014), and nanoparticulate aerosols (Faccini, *et al.*, 2012), air filter (Kakunuri, *et al.*, 2017; Chattopadhyay, *et al.*, 2015), sensor (Ding, *et al.*, 2010), biomedical and pharmaceutical materials for wound healing and drug delivery (Cremar *et al.*, 2018; Sridhar *et al.*, 2015).

2.1.2 Utilization of natural bio-polymer

Electrospinning process is a better opportunity for utilization of cellulose and its derivatives. Because, submicron to nano level diameter-based fiber can be easily obtained through this process. Bio-polymer such as cellulose usually has big challenges to processes. This is due to limited solubility in different organic solvents. Aggregation of cellulose in different solvents, is the serious problem to advance the of cellulose utilization. A few solvents are capable to dissolved cellulose and can be easily processed by electrospinning system. Among those N-methylmorpholine (NMMO)/water, lithium chloride/N, N-dimethylacetamide, and ionic liquids such as 1-allyl-3-methylimidazolium chloride (AMIMCl)/dimethylsulfoxide (DMSO) have been reported. Normally, those solvent has low volatility rate which leads to defective fiber upon electrospinning and also environmentally tedious and expensive. However, some of these solvents require high temperatures to completely dissolve cellulose. However, the residual ions effects completely remove is very difficult (Vallejos, *et al.*, 2012; Lee, *et al.*, 2009). Cellulose acetate is a semi-synthetic polymer obtained from esterification of pure cellulose with acetic anhydride using sulfuric acid as a catalyst reaction mechanism as shown in the **Figure 4-3**. The esterification degree depends on the substituted -OH groups by acetate groups. Cellulose acetate (CA), diacetate (CDA) or triacetate (CTA) is obtained in accordance with the esterification process. CA have many properties such as

weathering, heat and chemical resistance, thermal stability, toughness and dimensional stability (López-Velázquez, *et al.*, 2015). All of these properties make cellulose acetate attractive from the viewpoint of utilization of cellulose such as semi-permeable membranes for dialysis, ultra-filtration, reverse osmosis, affinity membrane, air filtration membrane, separation membrane (oil and water), etc.

In this chapter, electrospun fiber morphology and fiber diameters were investigated on aluminum foil for the use of further experimental process. Nevertheless, electrospinning can be alleviated by cellulose esters solutions followed by regeneration (saponification or alkali treatment). As an example, cellulose acetate can be easily dissolved and processed in non-polar solvent which is suitable for electrospinning such as ethanol, acetone, acetic acid, dichloromethane, chloroform and methyl acetate, etc. From these solvent lists, I consider the organic solvent ethanol, acetone, acetic acid and DMF from the viewpoint of low environmental harmful effect which might reduce the animal/human and safety risk. On the other hand, different organic solvent with different ratio of aqueous organic solvent was reported for microfiber preparation and their optimum CA concentration was also reported. All the electrospun fiber was deposited on the aluminum foil as a collector substrate material. The solubility of CA, fiber morphology (fiber surface especially roughness of fiber), fiber diameter is measured and finally, it was characterized for the next process.

2.2 Experimental

2.2.1 Materials

Water-soluble cellulose acetate (WSCA) with a degree of polymerization (DP) of 131 and degree of substitution (DS) of 0.9 and cellulose di-acetate (CDA) with a DP

of 181 and DS of 2.4 were kindly supplied from Daicel Corporation, Ltd., Japan. N, N-dimethylformamide (DMF), Acetone, Ethanol, Acetic acid and DMF were purchased from Wako chemical industries Ltd., Japan. Aluminum foil (0.1 mm in thickness, 99.99 % of purity) was purchased from local market. All chemicals were used as received without further purification. Stainless steel needle, glass syringe, needle cleaning tools and YMC syringe pump were purchased from YMC Co., Ltd, Kyoto, Japan.

2.2.2 Solubility check of WSCA and CDA in different solvent by electrospinning

2.2.2.1 Solubility of WSCA and CDA

Solubility is an important parameter for electrospun fibers preparation from cellulose derivatives such as cellulose acetate (CA). Therefore, solubility check is an essential subject for preparing of polymer solution before electrospinning from CAs (WSCA and CDA). This is because, proper solvent and their optimum ratio can produce optimum polymer solution. Only suitable ratio of proper solvent and CA concentration can produce continuous and beads free electrospun fiber from cellulose derivatives. For that reason, initially CAs (WSCA and CDA) were checked using pure different organic solvents with 100 % separately. The solvents were selected according to the concern of environmental friendliness such as- water, ethanol, acetone, acetic acid and DMF as shown in **Figure 2-1**. From the initial solubility result, WSCA and CDA were totally dissolved when organic solvent DMF is used for solution preparation. Therefore, fibrous morphology was not observed after electrospinning under 3D microscopic. Similar behavior also observed when the solvent acetic acid was used for CDA. On the other hand, WSCA was not dissolved in acetic acid.

Solubility of WSCA and CDA		
Solvent	WSCA	CDA
H ₂ O	Dissolved	Not dissolved
EtOH	Not dissolved	Not dissolved
AcOH	Not dissolved	Dissolved
Acetic acid	Not dissolved	Highly soluble (v)
DMF	Highly soluble (v)	Highly soluble (v)

Figure 2-1 Solubility checks list of WSCA and CDA with different solvents.

After preparing the polymer solution, transparent polymer solutions were subjected to electrospinning for fiber preparation. The solubility ck scheme for electrospun fiber preparation was shown in **Figure 2-2**.

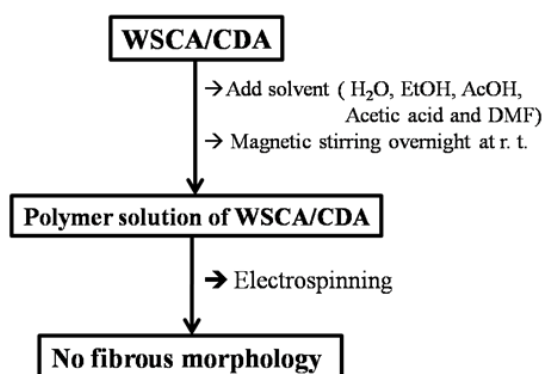


Figure 2-2 Electrospun fiber preparation strategy

There are different combinations of aqueous organic solvents such as ethanol and acetone, acetic acid and DMF were used, in which ethanol and acetone and their ratio are shown in the **Table 2-1**. This is because, other combination could not be able to give the formation of fibrous morphology due to high solubility of CA (WSCA and CDA) in acetic acid and DMF solvent system.

Table 2-1 Optimization of CA (WSCA and CDA) concentration and aqueous organic solvent ratio.

CA (WSCA) conc. (%)	Ratio : EtOH/H ₂ O										
	0	10	20	30	40	50	60	70	80	90	100
7	D	D	D	DF	DF	DF	X	X	X	X	X
9	D	D	D	DF	SF	NSF	X	X	X	X	X
11	D	D	D	DF	SF	NSF	X	X	X	X	X
15	D	D	D	DF	C	C	X	X	X	X	X
CA (CDA) conc. (%)	Ratio : Acetone/H ₂ O										
	0	10	20	30	40	50	60	70	80	90	100
7	X	X	X	X	X	X	D	D	DF	DF	DF
9	X	X	X	X	X	X	D	D	NSF	SF	NSF
11	X	X	X	X	X	X	D	D	NSF	NSF	NSF
15	X	X	X	X	X	X	D	D	C	C	C

X : Not soluble,
DF : Fiber with drop,
SF : Smooth fiber,
D : droplet,
NSF : Not smooth fiber,
C : High fiber diameter

2.2.2.2 Polymer solution preparation

The polymer solution was prepared by the following equation-

$$\frac{\text{Solute (g)}}{\text{Solute (g)} + \text{Solvent (g)}} = \%$$

Initially, WSCA polymer solution was prepared with 100 % of ethanol and CDA solution also prepared with 100 % of acetone for electrospinning. In case of WSCA, 1.2425 g of CA (WSCA:11%) powder was taken in a glass vial and then 10 g (w/w) of ethanol was poured in that glass vial. In case of CDA, in the same way 0.9915 g of (CDA: 9%) powder was also taken in a glass vial with 10 g of acetone. Both glass vial was placed on magnetic stirrer for stirring at 50 °C for overnight until clear solution. This clear polymer solutions were subjected for electrospinning.

2.2.2.3 Electrospinning on aluminum foil

As mention in materials and methods part, the aluminum foil about 35 cm length and 40 cm width was cut into pieces and then covered the grounded stainless-steel collector with that piece of aluminum foil. Two different kinds of cellulose acetates (WSCA and CDA) separately were electrospun on aluminum foil as collector substrate for their fiber morphology observation under 3D microscope.

2.2.2.4 Electrospinning process

About 2 ml of polymer solution was poured into a glass syringe which is connected with metal needle (22 G). The syringe was placed on the stage of syringe pump (YMC) for spinning where electrospinning parameter (applied voltage, needle inner diameter, distance between needle tip and collector, feeding rate etc) also consider for fibers preparation. The cellulose acetate (CA) solutions were inserted into a glass syringe with a stainless-steel needle (inner diameter, 0.70 mm), and then the syringe was set in an electrospinning apparatus manufactured at Machinery Laboratory, Graduate School of Science, Hokkaido University. After that, the syringe with nozzle and the collector were connected, the syringe was pressed with a syringe pump (YMC Co., Ltd., Kyoto, Japan) at a flow rate of 1.0 mL/h. The electrospinning conditions were as follows: distance between the nozzle and the collector, 10 cm; applied voltage, 18 kV; rotational rate of collector, 115 rpm; spinning temperature, 30°C; relative humidity, 22%. To control the humidity and the temperature, a dehumidifier and a room heater were used during spinning as shown in **Figure 2-3**.

2.2.2.5 Electrospinning of CA with different concentration

For the preparation of electrospun fibers, I considered the CA concentration from 7%, 9%, 11%, 15% and 17% for WSCA and CDA, respectively. WSCA was dissolved in 40 wt.% aqueous ethanol solutions to give its solutions at concentrations of 7-17% at 50 °C. CDA was dissolved in 90 wt.% aqueous acetone solutions to give its solutions at concentrations of 7- 17%. All polymer solutions were subjected to electrospinning. In the electrospinning setup, involves the application of a strong electric field to a droplet of a fluid, such as a melt or blend of polymer solution.

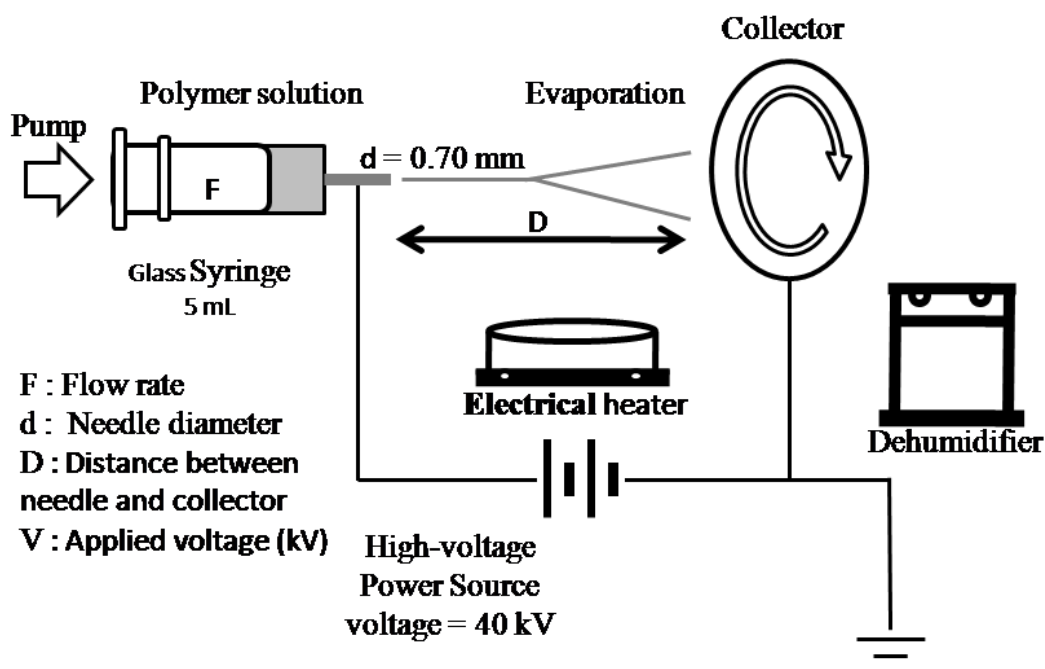


Figure 2-3 Schematic diagram of electrospinning set up to obtain random microfibers

The setup of electrospinning instrument mainly consists of a spinneret, stainless-steel grounded collector and high voltage power supply, room heater, dehumidifier, etc. The principle of electrospinning is a potential voltage (in kV) is applied between the needle tip and a collector; both are electrically conducting and separated at an optimum distance. The interactions of the electrical charges were created in the polymer solution with the external electric field, this external electric

field was form droplet on the top of needle tip from polymer solution into a conical structure which is named as Taylor cone. When the applied voltage surpasses the critical value of droplet of polymer solution, the repulsive electrostatic forces overcome the surface tension, a fine charged jet is ejected from the needle tip. These charged jets proceeded a whipping motion and elongate continuously through electrostatic force until they are deposited onto a grounded collector; as a result, fine fiber is obtained. If the applied external electrostatic field is not enough above the critical value, the result might cause the jet to into droplets. This is called Rayleigh instability. Therefore, nanofibers formation depends on the function of all operating parameters in proper way which is applied voltage, solution feeding rate and solution properties, solution conductivity, viscosity and surface tension. A schematic set up of an electrospinning apparatus as shown in **Figure 2-3**.

2.3 CA concentration

2.3.1 Water soluble cellulose acetate (WSCA)

The polymer solutions were prepared from WSCA, 7%, 9%, 11%, 13, 15% and 17 % of CA (WSCA) powder which was used as mention in the table 2-1 with aqueous organic solvent ratio of Ethanol/water: 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100%.

2.3.2 Cellulose diacetate (CDA)

Similarly, CDA polymer solution was prepared from the concentration of 7%, 9%, 11%, 13, 15% and 17 % of CDA powder which is describe in the table 2-1with above mention aqueous acetone (acetone/water: 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%,90% and 100%).

2.4 Characterization

2.4.1 Solubility check in 100 % organic solvent:

At first 100 % of organic solvent was used for solubility check of WSCA and CDA in organic solvent such as water, ethanol, acetone, acetic acid and DMF. **Figure 2-4** clearly shows the polymer solution appearance or solubility where WSCA dissolved in water and DMF. In case of CDA, it was dissolved in acetone, acetic acid and DMF.

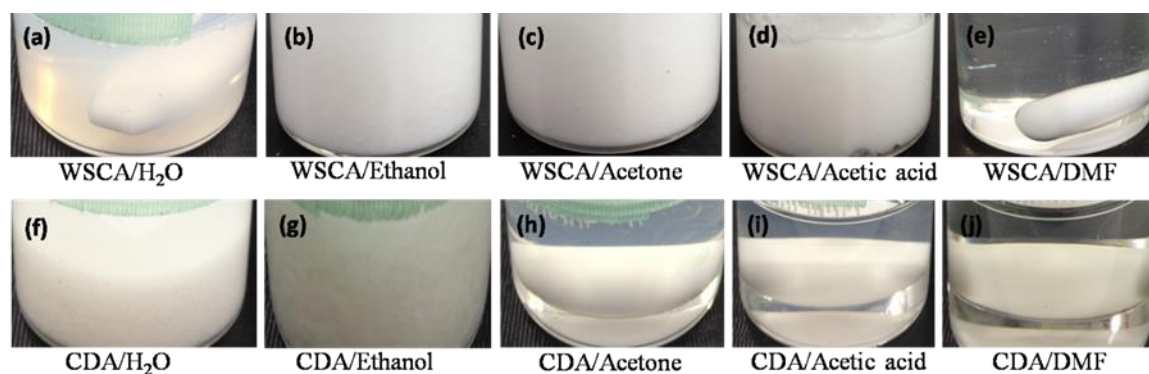


Figure 2-4 WSCA (11 wt.%) solution prepared from 100 % of (a) H₂O, (b) Ethanol, (c) Acetone, (d) Acetic acid and (e) DMF and CDA (9 wt.%) solution from 100 % of (a) H₂O, (b) Ethanol, (c) Acetone, (d) Acetic acid and (e) DMF.

2.4.2 Solubility check in different ratio with DMF:

For the solubility check of CA (WSCA and CDA), about 1.0 g of CA was taken in a glass vial and about 10 g (w/w) of organic solvent with different ration was poured into in a same glass vial. Finally, the glass vial was placed on a magnetic stirrer for stirring overnight at room temperature. After overnight mixing, the resultant mixture was looking transparent or turbid that was evaluating by normal eye observation. The transparent polymer solution was observed in case of both CAs (WSCA and CDA) as shown in **Figure 2-5**.

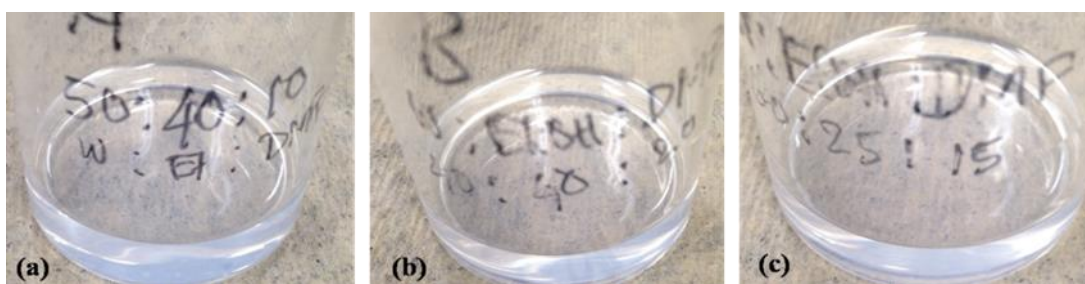


Figure 2-5 Solubility check of WSCA by using different ratio of solvent (a) water: ethanol: DMF (5: 4: 1), (b) water: ethanol: DMF (2: 2: 1) and (c) water: ethanol: DMF (12: 5: 3).

However, CAs (WSCA and CDA) was highly dissolved, when DMF was used as a solvent at any ratio. Thus, no fibrous morphology was observed using 3D microscope after electrospinning of both polymer solutions (WSCA and CDA). Therefore, DMF and acetic acid did not try for further polymer solution preparation.

2.4.1.2 Electrospun fiber morphology observation based on spinning condition

Spinning condition was controlled by controlling room temperature and air relative humidity (ARH). In this study, the optimum temperature and humidity range was about (30-33) °C and (22-25) %, respectively. Electrospinning parameter (applied voltage, needle inner diameter, distance between needle tip and collector, feeding rate etc) also consider for continuous, smooth and breads free electrospun fibers preparation.

The performance of electrospun fiber from 100 % of solvent and was observed under 3D microscope. **Figure 2-6.** shows that there was no clear fibrous morphology was observed when 100% acetone was used as an organic solvent in case of CDA **Figure 2-6 (C)**. On the other hand, WSCA was not dissolved in 100 % of ethanol

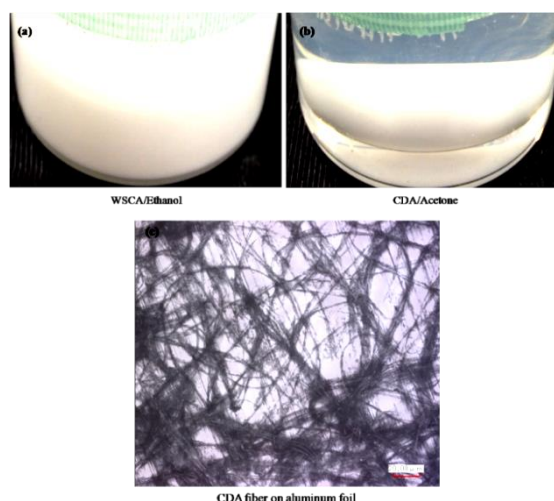


Figure 2-6 (a).

Figure 2-6 Organic solvent with 100% (a) WSCA and ethanol, (b) CDA with acetone and (c) Electrospun CDA fiber from 100 % of acetone

It was also clearly observed that only organic solvent cannot give long and beads free fiber. This is because, organic solvent has high volatilization rate. Therefore, organic solvents (ethanol and acetone) were easy to evaporate from the surface of electrospun fiber during spinning before fiber formation in the electrospinning system. As a result, defective fibers were observed. From the SEM analysis, **Figure 2-7** clearly shows the same fibrous morphology with beads. To suppress the high volatilization rate of organic solvent, I used water with organic solvent. Because, boiling point of water is comparatively higher than organic solvents. Therefore, in this study I used aqueous solvent system for controlling the evaporation rate of organic solvent.

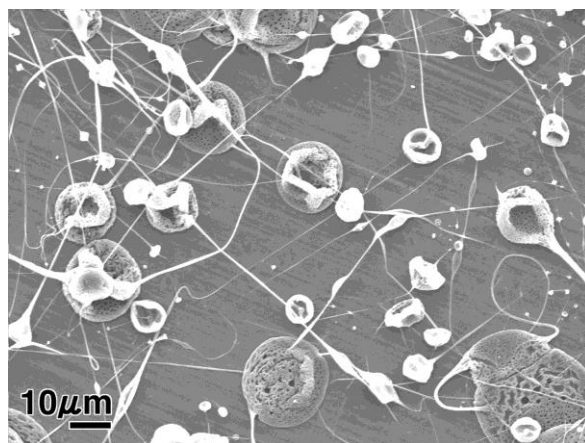


Figure 2-7 CDA electrospun fiber from 100% of acetone.

There are many ratios of aqueous solvent systems were used for smooth and fine electrospun fiber preparation. However, most of the combination of aqueous solvent did not give fine and elongated fibers. Desirable electrospun fibers were obtained from 40% ethanol and above for WSCA and 90 % acetone above for CDA.

Finally, I selected 40% of ethanol for WSCA and 90% of acetone for CDA of sub-micron electrospun fiber preparation. This is because, lower organic solvent ration could not form fiber only beads and higher ratio of organic solvent is the matter of cost for WSCA. On the other hand, higher amount of aq. organic solvent causes of beads instead of fiber, in case CDA. As shown in **Figure 2-7**, which was prepared from 100 % organic solvent acetone and the CDA fiber morphology was observed using SEM. The result SEM image is mostly shown beads due to 100 % of volatile organic acetone.

2.5 Result and discussion

2.5.1 Solubility check of WSCA and CDA in aqueous solvent system in DMF and acetic acid

According to the section 2.4.2, Water soluble cellulose acetate (WSCA) and cellulose diacetate (CDA) was dissolved in water: ethanol: DMF (5: 4: 1), water: ethanol: DMF (2: 2: 1) and water: ethanol: DMF (12: 5: 3). The polymer solution was

subjected to electrospinning. **Figure 2-8** clearly shows that electrospun fiber was not formed when DMF is used as a solvent for WSCA. This is because cellulose acetate highly soluble in DMF. Therefore, fibrous morphology electrospun fiber was completely disappeared at any concentration of DMF.

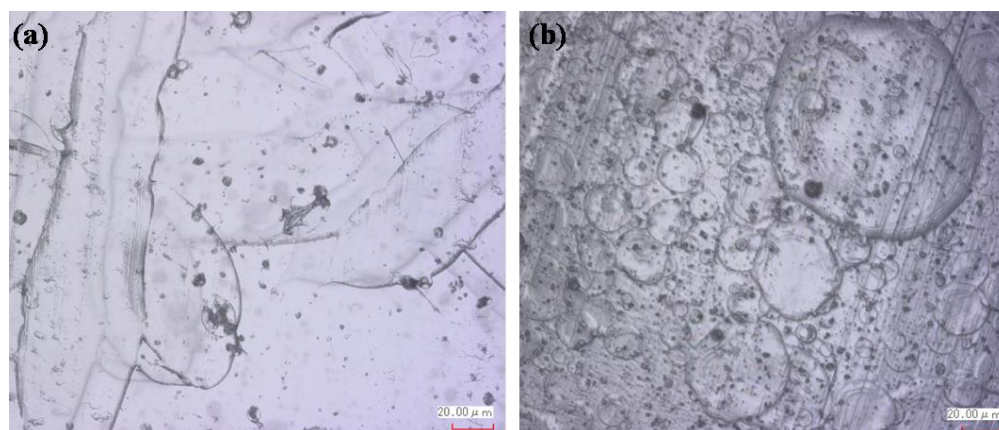


Figure 2-8 Electrospun fiber morphology of (a) WSCA (11 wt.%) and (b) CDA (9 wt.%) under 3D microscope with the solvent DMF.

Similar, behavior was also observed when I used acetic acid as a solvent. In the acetic acid solvent system also, no fibrous morphology was observed as shown in **Figure 2-9**.

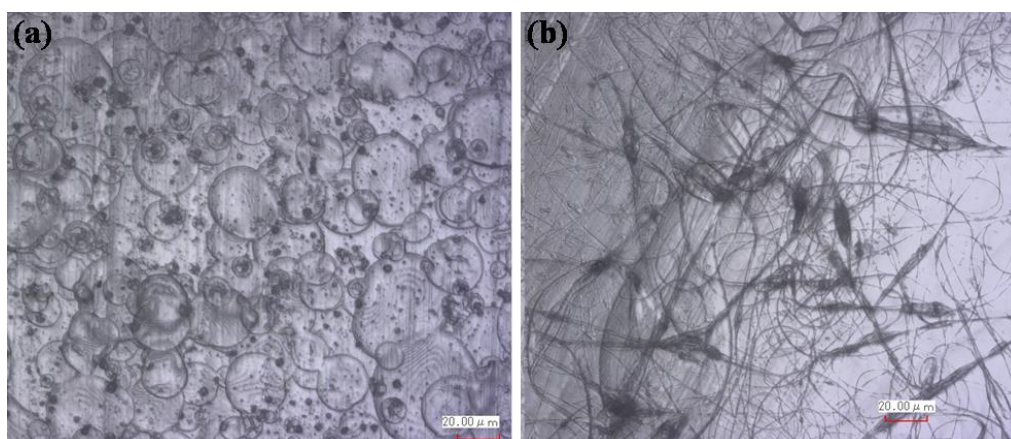


Figure 2-9 Electrospun fiber morphology of (a) WSCA (11 wt.%) and (b) CDA (9 wt.%) under 3D microscope with the solvent acetic acid.

Therefore, it can be concluded that DMF and acetic acid is not suitable solvent at any ratio for the electrospun microfiber preparation. Therefore, I selected aqueous ethanol for WSCA and aqueous acetone was selected for CDA polymer solution preparation for electrospinning. This is because, only aqueous ethanol and aqueous acetone can produce fine fiber through the electrospinning system. That's why, finally ethanol and acetone was selected separately for WSCA and CDA electrospun fiber preparation.

2.5.2 WSCA soluble in 100 % of water and DMF and CDA soluble in 100 % of acetone, acetic acid and DMF.

WSCA was dissolved in water (100 wt.%) and DMF (100 wt.%). Interestingly, it was not dissolved in ethanol (100 wt.%), acetone (100 wt.%) and acetic acid (100 wt.%) which were shown in **Figure 2-4**. The polymer solution of WSCA was prepared from water (100 wt.%) and DMF (100 wt.%) and CDA prepared from acetone (100 wt.%), acetic acid (100 wt.%) and DMF (100 wt.%) both (WSCA and CDA) polymer solution were subjected to electrospinning. **Figure 2-10 (a-e)** clearly shows that there is no electrospun fibrous morphology was observed.

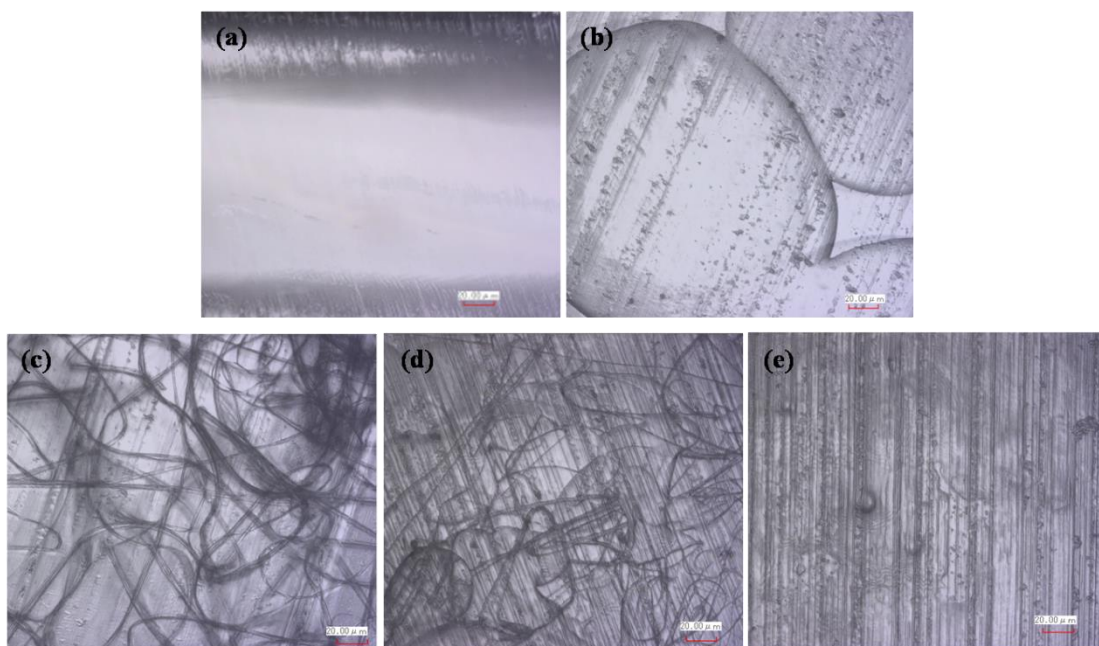


Figure 2-10 Electrospinning of WSCA polymer solution from water (100 wt.%) (a), DMF (100 wt.%) (b), CDA polymer solution from acetone (100 wt.%) (c), acetic acid (100 wt.%) (d) and DMF (100 wt.%) (e), respectively.

On the other hand, WSCA and CDA polymer solution were prepared from aqueous organic solvent system which solvent system could be able to produce fibrous morphology from CAs. This is because, boiling point of water is higher than most of the organic solvents. During solvent evaporation, CA fiber morphology was produced smoothly. Therefore, aqueous solvent system was introduced to suppress of organic solvent evaporation rate.

Interestingly, WSCA was not dissolved in ethanol (100%) but it was dissolved in aqueous ethanol at any concentration. Thus, homogenous polymer solution of WSCA was prepared from aqueous EtOH as a dope at concentration range for 7-17wt.%. WSCA solution was then subject to electrospinning. In this case, electrospun fiber could obtain from the solution concentration at 9-17% at an applied voltage 18 kV. It will be detailed describe in **chapter 3**.

3.5.3 Different CA concentration and fiber morphology of CAs (WSCA and CDA) with different aqueous solvent system.

The electrospun fibers were fabricated from the polymer solutions of WSCA and CDA. The stainless-steel collector was rounded by aluminum foil which was used as a collector for electrospun deposition. Different CAs concentration was chosen. From which, different concentration of CA fiber morphology was observed under 3D microscope. The result of fiber morphology as shown in **Figure 2-11**. There is no fibrous morphology was observed in acetic acid and DMF solvent system for both CAs.

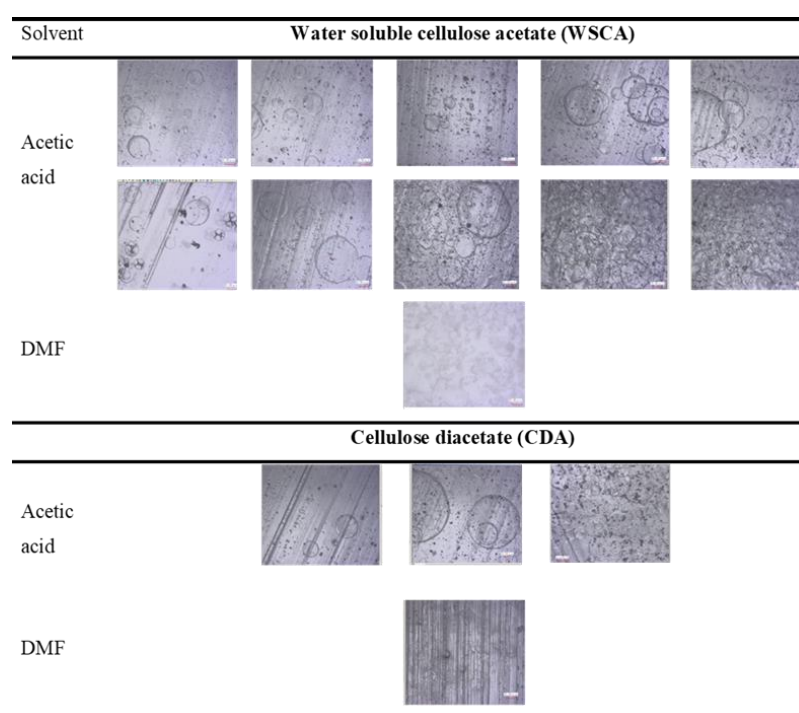


Figure 2-11 No fibrous morphology was observed after electrospinning of WSCA and CDA in different ratio of organic solvent acetic acid and DMF.

On the other hand, fibrous morphology formation was started under aqueous ethanol and aqueous acetone solvent from WSCA and CDA, respectively. In case of lower CA concentration makes beads whereas higher CA caused higher fiber diameter. Fiber formation was started from the CA concentration of 7 wt.% to 15 wt.% where 15 wt.% WSCA is caused by fiber diameter high (2.34 μm) and 5.69 for CDA. All

electrospun fiber diameter information's of WSCA and CDA were summarized in **Table 2-2**.

Table 2-2. Effect of CA concentrations on fiber morphology and diameter.

CA concentration (wt.%)	WSCA		CDA	
	Fiber morphology	Average diameter ¹⁾ (μm)	Fiber morphology	Average diameter ¹⁾ (μm)
1	only beads	-	only beads	-
3	only beads	-	only beads	-
5	only beads	-	only beads	-
7	fibers with beads	0.54 ± 0.07	fibers with beads	1.45 ± 0.51
9	fibers with beads	1.02 ± 0.05	uniform fibers	1.69 ± 0.52
11	uniform fibers	1.20 ± 0.05	uniform fibers	2.41 ± 0.71
13	uniform fibers	1.99 ± 0.62	uniform fibers	4.85 ± 0.69
15	uniform fibers	2.34 ± 0.52	uniform fibers	5.29 ± 1.20
17	uniform fibers	3.57 ± 0.59	uniform fibers	6.73 ± 1.69

¹⁾ Average fiber diameter $\pm$ standard deviation (SD).

The lower WSCA concentration (1-5 wt.%) yielded only beads (unsuccessful). The solutions at 7 and 9 wt.% yielded fibers and beads (unsuccessful). The solutions at 11 wt.% and higher concentrations gave uniform fibers (successful). In the concentration range of 11-17 wt.%, the fiber diameter was increased with an increase in WSCA concentration. Similarly, CDA conc. (1-5 wt.%) yielded only beads. The solution at 7 wt.% yielded fiber with beads. The solution at 9 wt.% and higher concentrations gave uniform fibers. The concentration range (9-17 wt.%), fiber diameter was increased with an increase in CDA concentration.

From the **Figure 2-12** shows that the fiber morphology with different concentration of WSCA (a) 7%, (b) 9%, (c) 11% and (d) 15%. In which, WSCA 11% of CA concentration with the solvent ratio of aqueous ethanol (2/3, w/w) was selected for the final sample preparation. Because, from this concentration of CA and aq. solvent ratio can produce smooth and fine fiber on PU sheet. The reason why, the optimum CA concentration can be produced desirable electrospun fibers. However,

optimum CA concentration and desirable fiber diameter is an important factor for surface modification of plastic sheet (PU sheet). In **Figure 2-12** shows the fiber morphology with different concentration of WSCA (a) 7%, (b) 9%, (c) 11% and (d) 15%. In which, WSCA 11% of CA concentration with the solvent ratio of aqueous ethanol solvent (2/3, w/w) was selected for the final sample preparation on PU sheet.

WSCA can be dissolved in aqueous ethanol at concentrations of 70 wt.% and under. In the case of CDA, it was dissolved in aqueous acetone at concentrations of 60-100 wt.%. Several solutions at different CA concentrations (7, 9, 11, 15 and 17 wt.%) and at different mixing concentrations of the aqueous organic solutions were prepared and subjected to electrospinning on an aluminum foil-covered collector. As a result, the electrospun fibers could be obtained from WSCA in 40 wt.% aqueous ethanol. For example, a solution at 7 wt.% of WSCA concentration gave both fiber and beads [**Figure 2-12 (a)**]. However, fine fibers were obtained from the solution at more than 9 wt.% [**Figure 2-12 (b)–(d)**]. WSCA solution at 11 wt.% concentration in 40%(w/w) aqueous ethanol yielded fine fibers with an average diameter of 1.20 ± 0.05 (SD) μm and smooth surface [**Figure 2-12 (c)**]. When, concentration was increased to 15 wt.%, the diameter of fibers increased to 2.34 ± 0.52 (SD) μm [**Figure 2-12 (d)**] these results are also consistent with the ones by previous paper ([Amiraliyan, et al., 2009](#); [Tarus, et al., 2016](#)). Therefore, the WSCA solution at 11 wt.% was used for the following experiments to obtain thin fibers.

Water soluble cellulose acetate (WSCA)

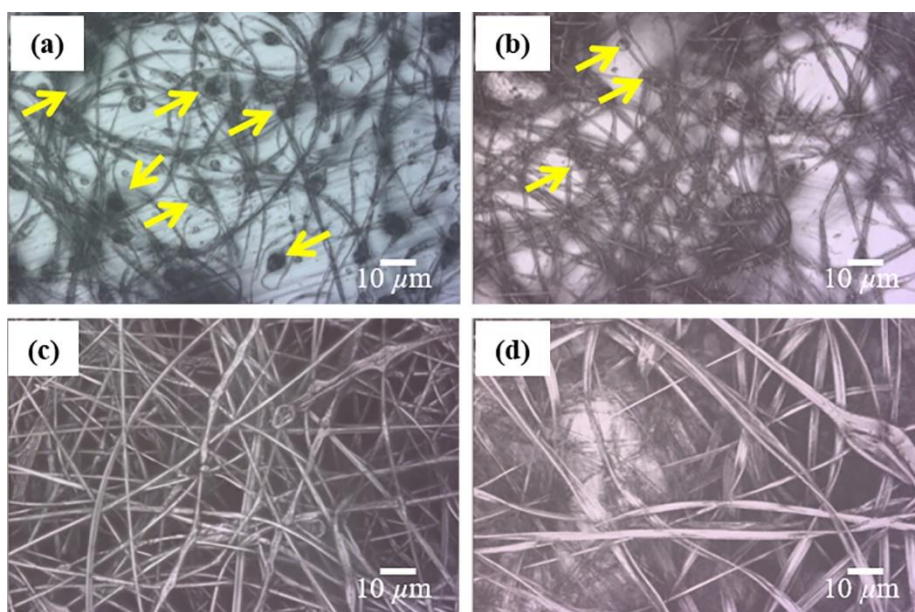


Figure 2-12 Morphology of electrospun fibers at (a) 7 wt.%, (b) 9 wt.%, (c) 11 wt.%, and (d) 15 wt.%, of WSCA concentrations in 40%(w/w) aqueous ethanol. An arrow shows droplet and beads.

On the other hand, **Figure 2-13** shows the CDA fiber morphology with different concentration of CDA (a) 7%, (b) 9%, (c) 11% and (d) 15%. Seven percent of CDA gave beads with fiber and 15% has high fiber diameter ($3.69 \mu\text{m}$). In which, CDA 9% of CA concentration with the solvent ratio of aqueous solvent (9/1, wt.) was selected for preparation of electrospun fiber, this is because, CDA 9% has smooth and long continuous fiber morphology. Therefore, this percentage and solvent ratio also used as a final CDA sample preparation on PU sheet.

In the case of CDA, the electrospun fibers were obtained from CDA at 90 wt.% of aqueous acetone. CDA solution at 7 wt.% concentration in the aqueous acetone gave both of fibers and beads [**Figure 2-13 (a)**]. Fine fibers were obtained from the solution at 9 wt.% and 15 wt.% [**Figure 2-13 (c) and (d)**], respectively. CDA solution at 9 wt.% yielded the finest fibers among the tested solutions with an average diameter of $1.69 \pm$

0.52 (SD) μm [Figure 2-13 (b)]. This solution conditions were applied to the following electrospinning experiments.

Cellulose diacetate (CDA)

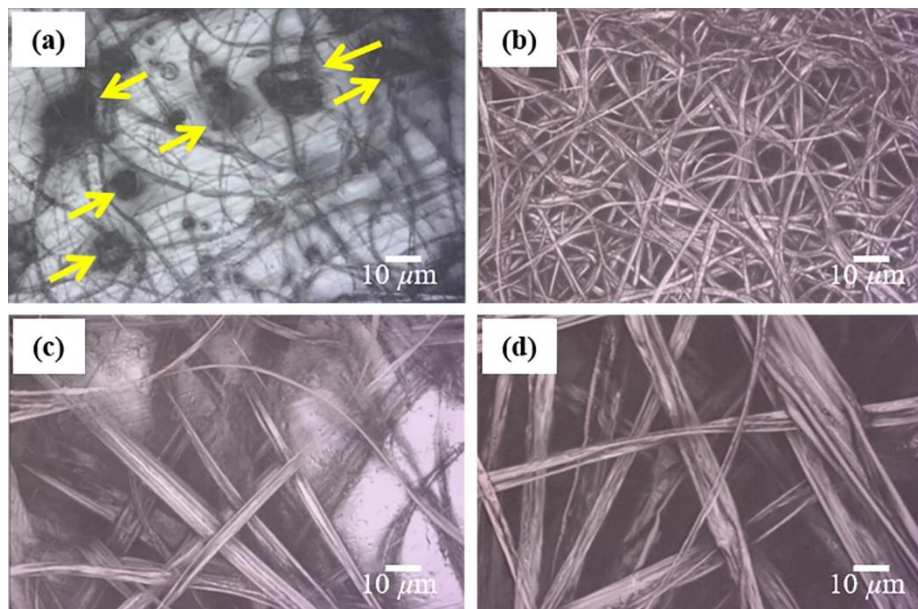


Figure 2-13 Morphology of electrospun fibers at (a) 7 wt.%, (b) 9 wt.%, (c) 11 wt.%, and (d) 15 wt.%, of CDA concentrations in 90 wt.% of aqueous acetone. An arrow shows droplet and beads.

The electrospun fiber preparation on PU sheet was detailed describe in the **Chapter 3** by using as above mention CAs concentration and solvent ratio.

Chapter 3 Preparation of CA fiber (WSCA and CDA) on electrically non-conductive Polyurethane (concave-convex) sheet through electrospinning

3.1 Introduction

Now-a-days, ultrafine fibers play a vital role including diameter range from nanometer to sub-micrometer due to their many sophisticated applied fields. There are different types of electrospun fiber are frequently produced from synthetic and bio-based polymers for different applications. Recently, bio-based materials production using natural polymer collected much attention. Because, sometimes it is an abundant and available after its major uses. These renewable resources are the major source of bio-based polymer. Ultra-fine fiber preparation could possible using one popularly method which known as an electrospinning process. Therefore, bio-based materials preparation through electrospinning is main target using natural renewable resources. Nanofibers produced from bio-polymer have special properties including high elastic property, low thermal expansion and light weight. In the fiber technology field, there are many applications of thin fibers such as medical application: drug delivery, wound healing; membrane application: filtration membrane, separation membrane, affinity membrane; sensor; etc from electrospun nanofibers. All most all electrospun fibers are deposited over aluminum foil as a collector or over porous synthetic surface such as nylon mesh as collector substrate. This is because, it is easy to create voltage difference between spinneret and collector plate.

Surface changes of plastic sheet (non-porous and non-conductive) through electrospinning is very difficult due to accumulation of static charge on over non-

conductive/insulator plastic surface. As a result, electrospinning is unsuccessful over plastic surface. In the electrospinning system, once it can easily fabricate nanofibrous mats on plastic surface (PU sheet) having high Young's modulus, low coefficient of thermal expansion, light weight, high specific surface area to volume ratio, high porosity and uniform morphology, it would be great option to open the new arena of cellulosic materials application by the electrospinning process. However, electrospinning on electrically insulator synthetic surface is limited. Additionally, the synthetic bio-based materials production strongly restricted due to electrostatic charge accumulation in the electrospinning process on non-conductive plastic surface (PU sheet). Synthetic materials along with several attractive properties of natural polymer could be able to mitigate the consumers increasing demand. It is also revealed that electrospinning on template assist on nylon mesh was intensively investigated ([Adepu et al., 2017](#)). Another research report also published that direct electrospinning of cellulosic material onto plastics was successful: cellulose acetate nanofiber was electrospun on nylon mesh as composite matrix for producing air filter ([Kakunuri et al. 2017](#)). This is because, voltage difference was easily created between needle tip and collector plate in porous nylon mesh. That's why, electrospinning is successful on nylon mesh.

As far I know, there is no report was published using bio-based materials preparation through electrospinning on an insulator plastic surface (PU sheet). If electrospinning process is successful on insulator plastic surface, it will open new the window for cellulose (abundant biomass) utilization and new technology-oriented bio-based material production and their application. At the same time, electrospinning process have found their way into different bio-based materials production and their application such as polishing materials for CD and HD. It is the main subject to

achieve wide operating system on the non-conductive plastic surface (PU sheet) with bio-based material production in the electrospinning field. Electrospinning and fiber fixation are the challenge on non-conductive plastic surface (PU sheet) because of static charge accumulation on insulator surface and peeling off property of electrospun fiber from synthetic surface. To overcome this problem, I prepared a strategy plan of electrospinning and at the same time fiber fixation on PU sheet during fiber preparation step as shown in **Figure 3-1**.

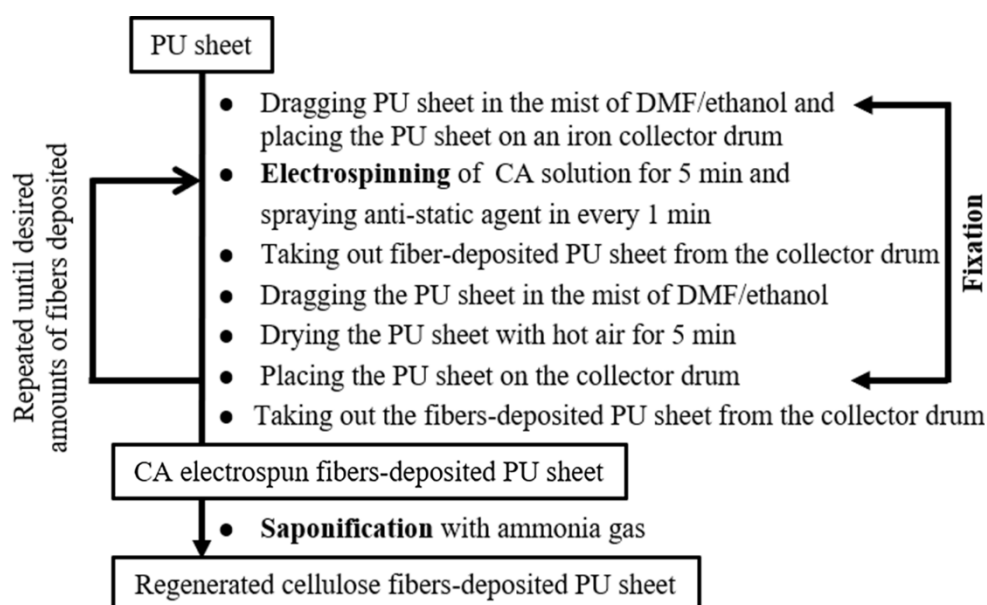


Figure 3-1 Preparation strategy of regenerated cellulose fibers-deposited PU sheet

Electrospun fiber preparation was detailed describe in the experimental part.

3.2 Experimental

3.2.1 Materials

Water-soluble cellulose acetate (WSCA) with a degree of polymerization (DP) of 131 and degree of substitution (DS) of 0.9 and cellulose di-acetate (CDA) with a DP of 181 and DS of 2.4 were kindly supplied from Daicel Corporation, Ltd., (Osaka,

Japan). N, N-dimethylformamide (DMF), Acetone, ethanol, acetic acid and aqueous NH₃ (28%) were purchased from Wako Pure Chemical Ltd., (Tokyo, Japan). Glass vial, spatula, glossy paper, magnetic stirrer and forceps were purchased from Wako Pure Chemical Industries, Co., Ltd. in Japan. An anti-static agent (staticide: 99.8 % of anhydrous isopropyl alcohol) was purchased from ACL Inc. (Chicago, IL, U.S.A.). Stainless steel needle, glass syringe, needle cleaning tools and YMC syringe pump were purchased from YMC Co., Ltd, Kyoto, Japan. Electrospinning apparatus was manufactured by Graduate school of Engineering faculty, Hokkaido University, Japan. DMF and ethanol (EtOH) were used as a mixed solvent at a ratio of 1:1 (w/w). The resulting solution is abbreviated to DMF/ EtOH (1/1). As a polishing pad for compact disc (CD) and hard disc (HD), polyurethane (PU) sheet with poly(ethylene terephthalate) (PET) as a supporting film was provided by Fujibo Ehime Co., Ltd.(Saijo, Japan).

3.2.2 Electrospinning WSCA and CDA polymer solution on PU sheet as a collector

3.2.2.1 Polymer solution preparation

Polymer solution was prepared according to the section 2.2.2.2. of **Chapter 2**.

3.2.2.1.1 Electrospinning of Water-soluble cellulose acetate (WSCA)

WSCA powder was measured with balancer. The amount of CA was calculated by the following equation.

$$\frac{\text{Solute (g)}}{\text{Solute (g)} + \text{Solvent (g)}} = \%$$

The amount of CA 0.9934 g (about 9%) of WSCA powder was taken in a glass vial. Aqueous solution with the ratio of ethanol/water (2/3, w/w) or 40 wt.% of ethanol and 60 wt.% of water were poured in a same small glass vial (mL) that had been already calculated amount of CA (WSCA) powder. Finally, the air tight glass vial was placed on a magnetic stirrer at 50 °C for overnight until clear polymer solution preparation.

About 2 mL of polymer solution was poured in a glass syringe with metal needle (22G) where inner diameter of metal needle was 0.70 mm. The syringe with polymer solution was placed on the syringe pump panel. Finally, syringe pump with polymer solution loaded syringe was placed on the electrospinning set-up board as shown in **Figure 3-2**. Polyurethane sheets were placed on the grounded collector as a substrate material. Finally, Electrospinning was started with the help of high voltage power generator (about 38 kV). Atmospheric condition (temperature and air relative humidity), feeding rate of polymer solution, distance between needle tip and collector plate, needle inner diameter, applied voltage, rotational speed of collector drum etc were controlled during spinning. An anti-static agent was evenly sprayed once on PU sheet for a few seconds before spinning and once in every 1 min during spinning.



Figure 3-2 An electrospinning setup view

3.2.2.1.2 Electrospinning condition and usefulness of spraying anti-static agent

In this study, before electrospinning, room atmospheric condition was maintained by using room heater for temperature and dehumidifier for humidity controller. The temperature and air relative humidity was maintained 29-35 °C and 22-25%, respectively. To control the humidity and the temperature, a dehumidifier and a room heater were used before and during spinning.

The cellulose acetate (CA) polymer solutions were inserted into a glass syringe with a stainless-steel needle (inner diameter, 0.70 mm), and then the syringe was set in an electrospinning apparatus manufactured at Machinery Laboratory, Graduate School of Science, Hokkaido University. The syringe nozzle and the collector were connected, the syringe was pressed with a syringe pump (YMC Co., Ltd., Kyoto, Japan) at a flow rate of 1.0 mL/h. The electrospinning conditions were as follows: distance between the nozzle and the collector, 10 cm; applied voltage, 18 kV; rotational rate of collector, 115 rpm; spinning temperature, 30°C; relative humidity, 22%.

Electrospinning of WSCA and CDA on the PU sheets, which were rolled in parallel on the iron collector, was attempted using the optimized solutions of WSCA and CDA as mentioned above. After electrospinning spinning was started, a few second latter electrospun fiber deposition directions were changed even though, initially fiber deposition were carried out on PU sheet. It was assumed that this phenomenon was occurred due to accumulation of static charge on the insulator surface of PU sheet where electro potential difference was disappeared. Electrospun fibers were deposited on the PU sheets only for initial 2 min. Afterwards, the fibers were deposited outside of the PU sheets, especially, on the non-covered surface of the iron collector between PU sheets, as shown in **Figure 3-3 (a) and (b)**. It was assumed that PU sheets were an electric insulator, and static charge was accumulated on the sheet during electrospinning, leading to unsuccessful electrospinning. One simple method is applied to reduce the potential difference between needle tip and collector plate by using anti-static agent in the electrospinning process. This process is quite simple and economical; thus, it has become the preferred method of choice for microfiber preparation. Electrospinning involves a high voltage being applied on a contained polymer solution to create electrically charged jets of solution that could be accelerated through a spinneret toward a grounded target which acts as a collector. An anti-static agent was evenly sprayed once on PU sheet for a few seconds after spinning and once in every 1 min during spinning.

In this chapter, I select staticide to remove the static charge from the PU surface. The staticide was used during spinning for fiber deposition target change from metal collector to the insulator surface. Otherwise, electrospun fiber deposition direction had been mostly onto the metal collector. The result of electrospun fiber deposition direction was observed normally on the PU surface due to successfully

remove the static charge from insulator surface. To remove the static charge, anti-static agent was sprayed several times on the sheets during electrospinning. By this treatment, both CA fibers were successfully deposited on the PU sheets **[Figure 3-3 (c)]**. This method of spraying anti-static agent was applied to other synthetic polymer sheets, such as polyethylene and poly(methyl methacrylate) sheets. As a result, this spraying method was found to be an effective in direct electrospinning of CA fibers on any synthetic polymer sheet. As shown in the **Figure 3-3**.

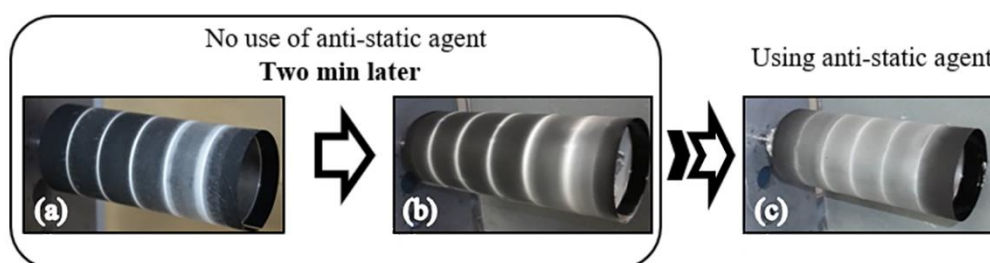


Figure 3-3 Electrospun fibers deposited on the PU sheets (a) for initial 2 min, (b) 2 min thereafter and (c) with an anti-static agent.

3.2.2.1.3 Cellulose diacetate (CDA)

In case of CDA polymer solution preparation was followed as above-mentioned procedure in the same manner of section 2.2.2.2 and 2.2.2.3 in **Chapter 2**.

3.2.3 Electrospun fiber fixation with PU sheet using mixed solvent treatment during spinning

It was clear that electrospinning of CAs were successfully carried out on electrically insulator synthetic surface using anti-static agent during spinning. However, another problem arose: the resulting electrospun CA fibers were easily peeled off from PU sheet by rubbing with a finger. This is because of the PU sheet is amorphous and cellulose is partly crystalline. Therefore, no chemical reaction was happened between

polyurethane sheet and crystalline cellulose. For that reason, electrospun CA fiber easily peeled off from PU surface which was clearly observed after using durability test by rubbing with finger as shown in **Figure 3-4 (a)**.

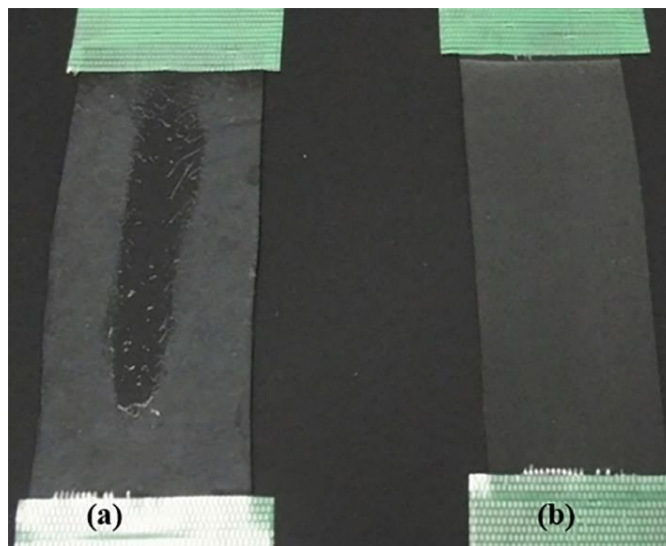


Figure 3-4 Durability test by rubbing with a finger on a PU sheet covered with electrospun CA fibers (a) before and (b) after mixed solvent treatment.

To overcome this problem, I changed a strategy for fixation of electrospun fibers on the PU sheets by using mixture of (DMF/ethanol) solution. This is because DMF is a good solvent for PU sheet and CA fibers. Therefore, it was attempted to be sprayed, to partly dissolve both materials to fuse them each other. When DMF was directly sprayed to the sheets, the electrospun fibers on PU sheets were almost dissolved, as shown in **Figure 3-5**. There were different ratios of DMF and ethanol solution mixtures were used by using domestic sprayer (watering plant). Most of the cases fiber morphology was lost **Figure 3-5 [(a) 90%, (b) 80%]** when DMF ratio was increased from 40 to 100%. On the other hand, less amount of DMF solution cannot fix the fiber tightly with PU sheet. Electrospun fibers could be tightly fixed with the range of DMF solvent 50 to 60 % ethanol. Therefore, I select 50% DMF solvent for electrospun fiber fixation with PU sheet in this study. **Figure 3-5 [(d) 50%]** shows the

electrospun CA fiber fibers morphology from 17% of CDA after fixation with 50% DMF/ethanol mixture.

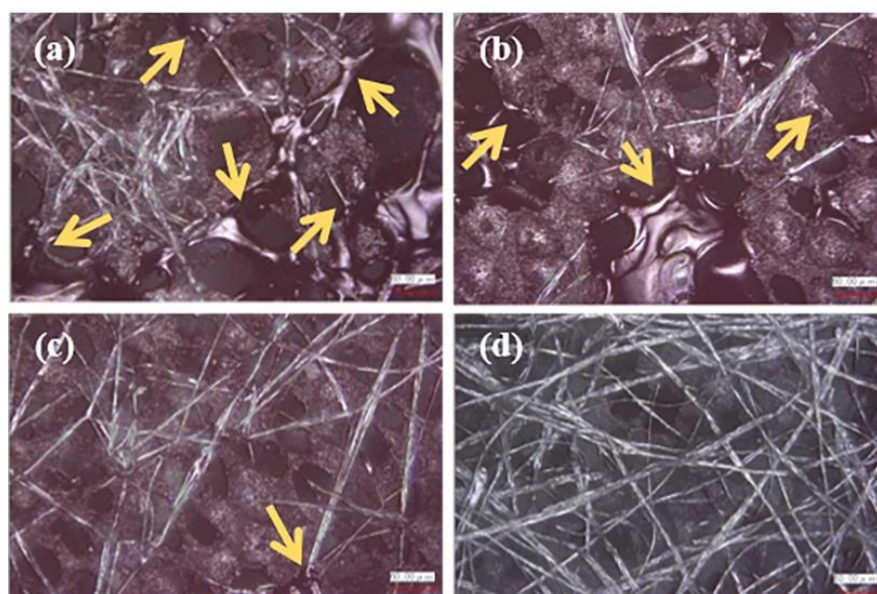


Figure 3-5 Electrospun fiber morphology of CDA 17 wt.% concentration fixed with 90% (a), 80% (b), 60 % (c) and 50 % (d) DMF solution spray, respectively. Arrows show the dissolving part of fibers and PU sheet.

Thereby, a mixed solvent of DMF/EtOH (1/1, w/w), as a poorer solvent system, was applied to dilute DMF. The fiber-coated PU sheets were dragged in the mist which was prepared by spraying a mixed solvent of DMF/EtOH (1/1, w/w) for 1 sec $\times$ 3 times. As a result, electrospun fibers were partly fused with PU sheets, and electrospun CA fibers were not peeled off easily from the PU sheet by rubbing with a finger **Figure 3-4 (b)**. For the further confirmation of fibers fixation, tribology test was carried out by tribogear instrument before and after fixation with different loading conditions. The result was shown in **Figure 3-6**. From the external appearance of PU sheet, it is clear that non-fixed sample easily peel off with minimum load (5 gf) before fixation as shown in **Figure 3-6 (a)**. Whereas, it was unchanged even loading amount was 150 gf with 20 reciprocation times **Figure 3-6 (b)**.

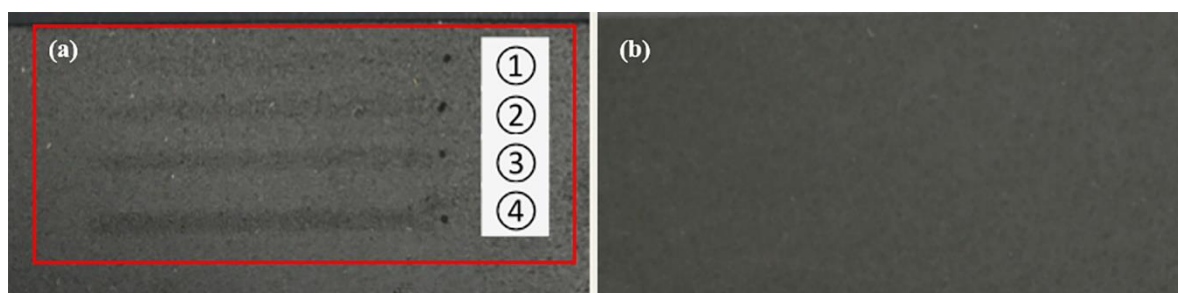


Figure 3-6. Fiber adhesion strength roughly estimated with tribology test machine before (a) and after (b) the fixation treatment with DMF/ethanol solution.

(a - 1, 2, 3 and 4), rubbing test under 5 gf loading at one-time scan (back-and-forth motion), at three-time scans, at six-time scans and at twelve-time scans, respectively.

(b), rubbing test under 150 gf loading at twenty-time scans.

On the other hand, fiber fixation process was attempted using DMF/Ethanol (1/1) before and after electrospinning, both processes were not succeeded. Therefore, electrospinning and fiber fixation were carried out during spinning. Mixed solvent was sprayed according to procedure 1 and based on the strategy plan of **Figure 3-1** in **Chapter 3**. As a result, electrospun fiber fixation with PU sheet was achieved.

3.2.4 Determination of electrospun fiber deposition amount on PU sheet

Amount of fiber deposition was measured by spinning of different amount of polymer solution on PU sheet. In this experiment, before electrospinning, the PU sheet was cut into small pieces about $30.30\text{ cm} \times 3.97\text{ cm} = 114.837\text{ cm}^2$. These small pieces of PU sheet were vacuum drying at $60\text{ }^{\circ}\text{C}$ for overnight and then cool down at room temperature in desiccator. The weight of PU sheet was measured after cooling down at room temperature by using four digits balancer (**W₁**). Finally, this PU sheet was tightly placed on collector with double side tape for electrospinning as shown in

Figure 3-7. After spinning, electrospun CA fiber coated PU sheet was placed in vacuum drying chamber for drying at 60 °C for overnight. After drying, it was cooled in desiccator at r.t. (**W₂**). This difference is the fiber amount on PU sheet (**W₂ – W₁**).



Figure 3-7 PU sheet placed on collector plate with double side tape

The amount of prepared polymer solutions as mention before in **chapter 2** were poured into a glass syringe connected with metal needle. The syringe with polymer solution was placed on YMC syringe pump panel which had been already placed on electrospinning instrument. This amount of solution was completely sprayed on PU sheet by applying anti-static agent during electrospinning. Initially, fiber amount was calculated on A4 sheet after that it was converted into **g/m²** by using the following equation.

$$\text{Amount of fiber} = \frac{\text{Amount of fiber on PU sheet (mg)}}{\text{Area of PU sheet (cm}^2\text{)}} \times \frac{10,000 \text{ cm}^2}{1 \text{ m}^2}$$

Different amount of spraying polymer solution and fiber amount on PU sheet was calculated. The results were compiled in the **Table 3-2** for WSCA and in **Table 3-3** for CDA in result and discussion section of this chapter (**Chapter 3**).

3.2.5 Preparation of regenerated cellulose fiber from CA fiber through saponification

In this part, the chemical properties of the fabricated electrospun microfiber were determined by adsorbing carbonyl ester group and go on to characterize their physical attributes. There are many methods for deacetylation of cellulose acetate such as NaOH/EtOH, NaOH/NaCl, NH₃ aqueous solution etc, in which NH₃ aqueous solution was chosen in this study. Because, when I used other solvent (NaOH/EtOH or NaOH/NaCl), PU and PET was also separated from each other. This result is not fulfilling our main objective. Therefore, NH₃ vapor or gas is important for saponification treatments to obtain regenerated cellulose fibers.

3.2.5.1 Saponification procedure of electrospun WSCA and CDA electrospun microfiber

Part of WSCA/CDA fiber-coated PU sheet [(3.79 cm × 6 cm; 1.84 mg), (3.79 cm × 6 cm; 3.366 mg) and (3.79 cm × 6 cm; 7.28 mg) WSCA/CDA was contained] was cut with a pair of scissors and put in a petridish (i.d. 8.5 cm) with a pair of tweezers. No top was on the petridish. Aqueous NH₃ solution (28wt%, 25mL) was poured in another petridish (i.d.8.5 cm), using a measuring cylinder and a Pasteur pipette. No top was on the petridish. This process was done in a fume hood because NH₃ is a pungent reagent. Those two petridishes were placed together in a larger petridish (i.d. 20.0 cm). The larger petridish was covered with a top. The larger petridish with a top was sealed with parafilmTM and then cling film (SalanTM Wrap), in order to avoid NH₃ leakage. Then, WSCA/CDA was saponified under an NH₃ atmosphere. The petridish was left standing at room temperature for 7 days. The saponified WSCA/CDA-coated PU sheet was taken out of the petridish and washed well with a large amount of distilled water. The PU sheet was dried in desiccator by using pump at room temperature for overnight.

Thus, WSCA/CDA fiber coated PU sheet was subjected to FTIR (ATR) analysis to check of ester carbonyl band (around 1700-1750 cm^{-1}). Finally, FTIR (ATR) band and X-ray diffraction patterns were measured only electrospun fiber which is produce from CAs (WSCA/CDA) on aluminum foil. This is because; band of carbonyl ester group was overlapped when it was measured with PU sheet. Therefore, FTIR (ATR) and XRD measurement's samples were prepared on aluminum foil.

3.2.5.2 Characterization of saponified fiber

3.2.5.2.1 FTIR (ATR) spectra measurement

ATR-FTIR is a useful technique to investigate the functional groups of cellulose microfibers (Ma and Ramakrishna, 2008). **Figure 3-17** shows spectra of PU sheet (a), cellulose acetate (CDA) fiber (b), cellulose acetate (WSCA) fiber (c), regenerated cellulose (CDA) fiber (d), regenerated cellulose (WSCA) fiber (e) and filter paper (f). **Figure 3-18.** shows the x-ray diffraction patterns of cellulose acetate (WSCA and CDA), regenerated cellulose (WSCA and CDA) microfibers and intact PU sheet.

3.2.5.2.2 X-ray diffraction pattern measurement

X-ray diffraction profiles of CA fiber and the regenerated cellulose fibers were performed using Powder X-ray diffraction (Rigaku, Japan) with $\text{Cu-K}\alpha = 0.154 \text{ nm}$ at 45 kV and 40 mA. The distance between the detector and the sample was 117 mm. The wavelength of the X-ray beam ($\text{Cu-K}\alpha$) was $\lambda = 1.54 \text{ \AA}$. The beam was calibrated using silver behenate standard with the first reflection peak at the scattering vector $q = (4\pi \sin \theta)/\lambda = 1.076 \text{ nm}^{-1}$, where, θ is the scattering half-angle. X-ray Diffraction (XRD) data were analyzed with six-point model followed by the following equation.

$I(2\theta)$

$$= \frac{\left[-21I(2\theta i - 4) + 14I(2\theta i - 3) + 39I(2\theta i - 2) + 54I(2\theta i - 1) \right. \\ \left. + 59I(2\theta i) + 54I(2\theta i + 1) + 39I(2\theta i + 2) - 14I(2\theta i + 3) - 21I(2\theta i + 4) \right]}{231}$$

And curve or peak fitting model was used to deconvolute the crystalline and amorphous regions of the crystalline cellulose.

3.2.6 Characterization

3.2.6.1 Electrospun fiber fixation process

Electrospun fiber fixation process was carried out in different ways such as heating PU sheet with electrospun fiber by using hot plate, direct spraying mixed solvent on CA fiber coated PU sheet, different ratio of DMF/EtOH solution spray and different process of mixed solvent spray during spinning before and after spinning. As shown in **Figure 3-5** electrospun fibers were mostly dissolved in highly concentrated DMF solution. When CA fiber coated PU sheet is heated with the temperature range 90 to 120 °C the PU sheet was melted. Thus, these processes were not suitable for electrospun fiber fixation with PU sheet. However, lower concentration of DMF with ethanol could bring good fixation fiber morphology but, in that case, solvent ratio is important. Therefore, mixtures of different ratio of DMF/EtOH were tried (90 %, 80 %, 60 % and 50 % of DMF) for CA fiber fixation. In most of the cases, fibers has lost their morphology and PU sheet surface also changed as shown in **[Figure 3-5 (a), (b), (c)]**. Whereas, mixture of DMF/EtOH (1/1, w/w) solutions can kept the fibrous morphology of electrospun fibers after mixed solvent treatment during spinning as shown in **Figure 3-8**.



Figure 3-8 Fiber morphology after mixed solvent DMF/EtOH (1/1, w/w) treatment on PU sheet.

Therefore, tightly fixed fiber preparation on PU sheet were carried out with DMF/EtOH (1/1, w/w) treatment. Now, problem is mixed solvent spraying methods. When above mention ratio was used after spinning on PU sheet at that time fiber was not tightly fixed also it contained many droplets of mixed solvent. Therefore, I selected to use mist of mixed solvent by using domestic sprayer (watering plant) during spinning. In this case, mist of mixed solvent was sprayed following procedure in procedure 1(a) and procedure 2 (b).

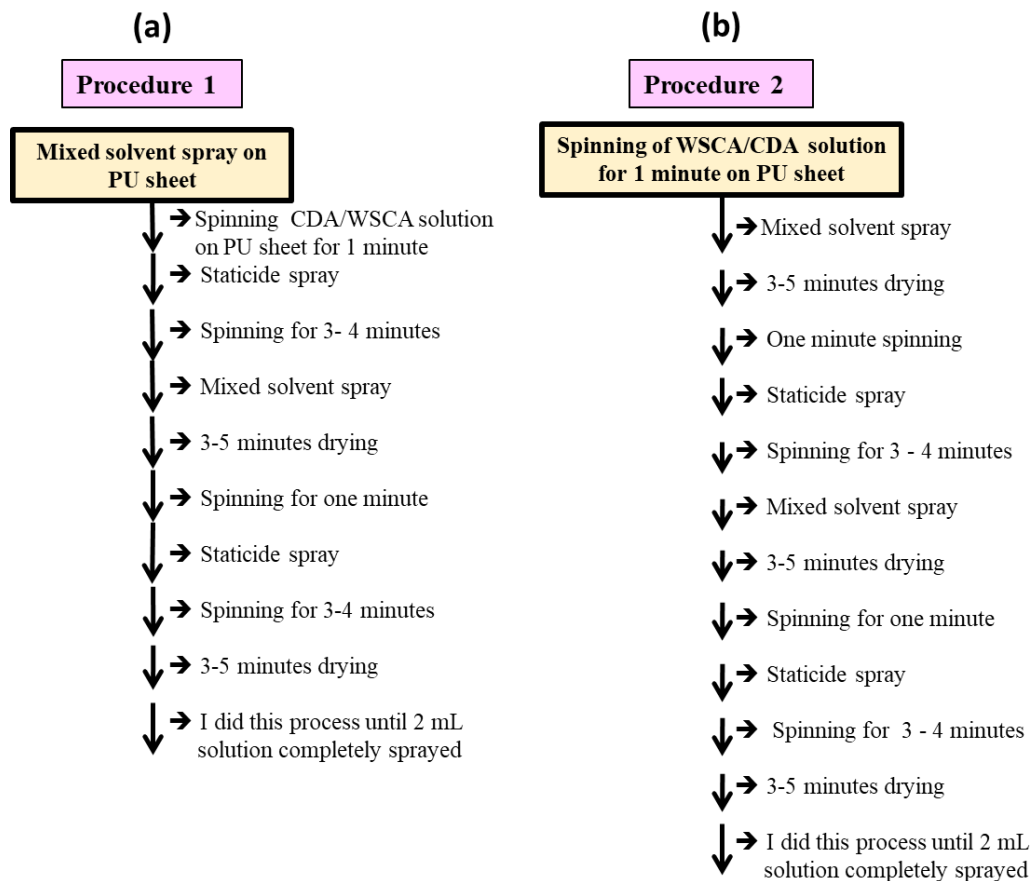


Figure 3-9 Mixed solvent spraying flow chart for electrospun CA fiber adhesion and/or prevent from peeling off from PU sheet with procedure 1 (a) and procedure 2 (b) during spinning.

For procedure 1:

In this process, the use of mixed solvent was carried out at the spinning time. At first, I sprayed mixed solvent onto air. An intact PU sheet was carried in the mist of the mixed solvent just before spinning. Then it was placed on collector plate for 1 min spinning, and then I sprayed anti-static agent on PU sheet during spinning. The spinning process was continued upto three to four minutes then I carefully taken out the PU sheet from the collector plate. The CA fiber coated PU sheet was dragged in the mist of mixed (DMF/Ethanol: 1/1) solvent and the CA fiber coated PU sheet was dried

for 5 minutes by using hair dryer. And again, I placed the CA fiber coated dry film on collector plate and the same process, I repeated until completely spinning of 2 mL of polymer solution [Figure 3-9 (a)]. The resultant film was dried *in vacuo* condition for overnight at room temperature and fiber morphology on PU sheet was observed under 3D microscope as shown in Figure 3-10.

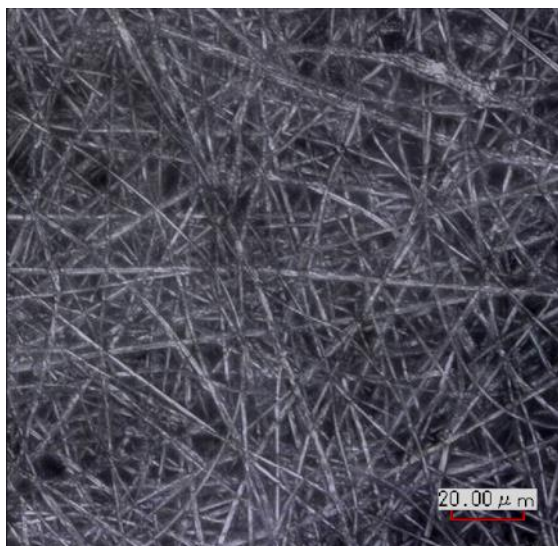


Figure 3-10 CA fiber morphology after mixed solvent treatment during spinning with the process1.

For procedure 2:

In this process, at first, I placed an intact PU sheet on collector drum and I started spinning for one minute without use of the anti-static agent and/or mixed solvent then I carefully taken out the PU sheet from the collector. After that, I sprayed mixed solvent onto air and then 2 seconds later, the CA fiber coated film was carried out in the mist of mixed solvent. The mixed solvent on PU sheet was dried for 5 minutes by using hair dryer. It was placed on collector drum, and I sprayed anti-static

agent on PU sheet after one-minute spinning during spinning. Totally, five minutes spinning in one span before drying, Anti-static agent was sprayed at every one minutes interval during spinning. And the PU sheet was carefully taken out from the collector drum and dried it for 5 minutes by using hair dryer. Again, I placed the fiber coated film on collector drum and the same process I repeated until completely spinning of 2 mL of polymer solution **[Figure 3-9(b)]**. The resultant film was dried *in vacuo* condition for overnight at room temperature and fiber morphology on PU sheet was observed under 3D microscope.

Procedure 1(a) is more suitable than procedure 2 (b) because, electrospun fiber can easily fused with intact PU sheet by the help of mixed solvent mist when mixed solvent mist was sprayed before spinning. Finally, I selected the procedure 1 to prevent the fiber peeling off properties from PU sheet. As a result, electrospun fibers were closely adhered with PU surface through procedure 1 which is strongly suggested the SEM images as shown in **Figure 3-11**.

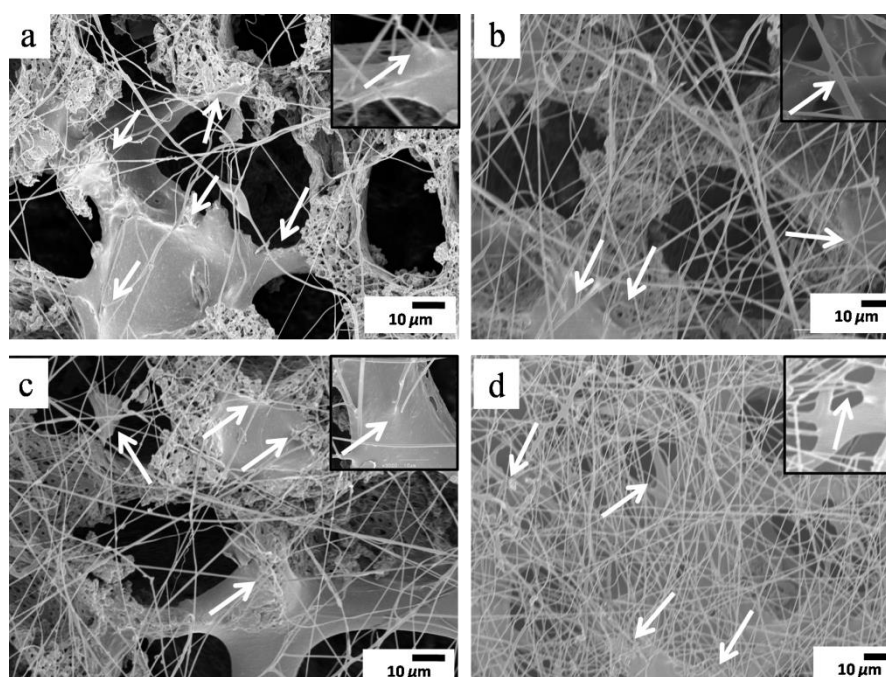


Figure 3-11 SEM images of different amount of CA fiber deposition on PU sheet (a) 0.81 g/m² (b) - (c) 1.61 g/m² and (d) 3.20 g/m² by using mixed solvent treatment. Arrows indicate fused parts of electrospun CA fibers and PU sheet.

3.2.6.2 Deposition amount of electrospun CA fiber on PU sheet

As describe in section 3.2.4, the polymer solutions were completely spinning on PU sheet by spraying anti-static agent and mixed solvent treatment during spinning. Different amount of electrospun non-fixed and fixed fibers deposited PU sheet sample were shown in **Figure 3-12**.

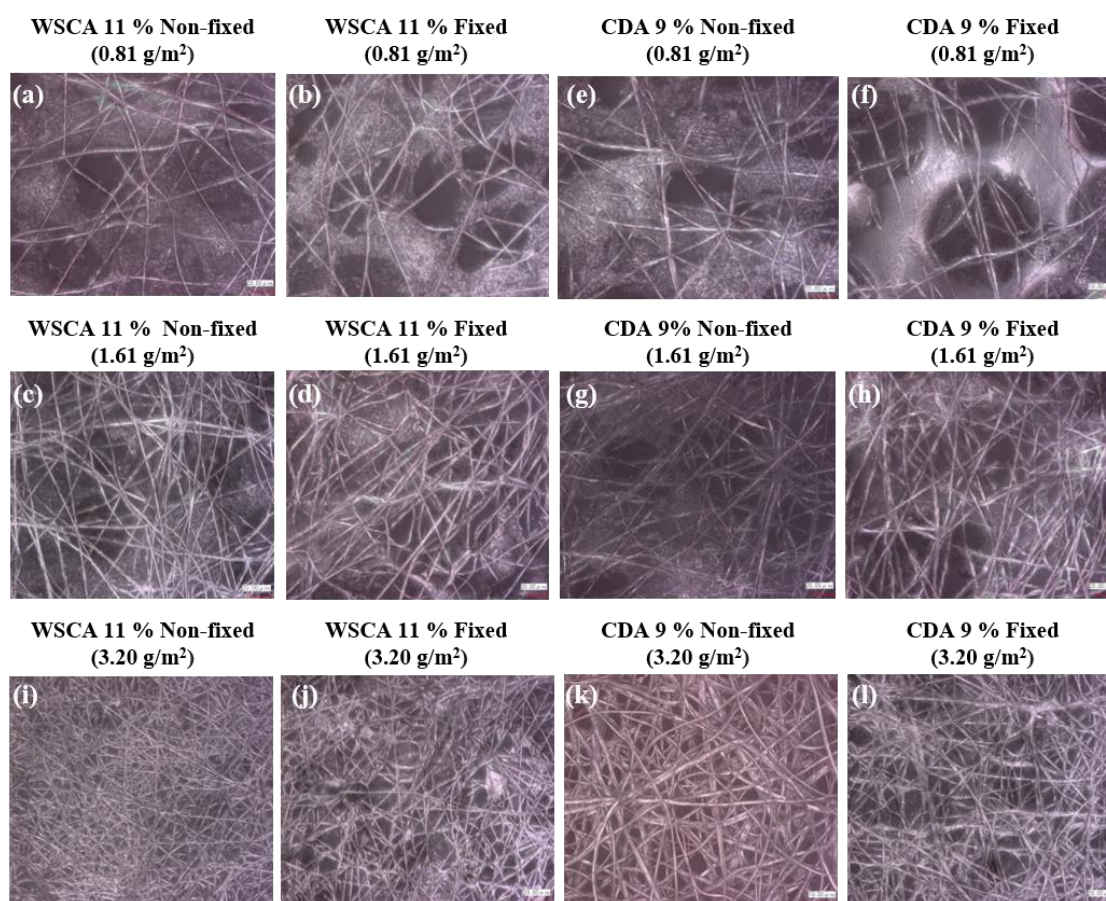


Figure 3-12 Fiber morphology observed under 3D microscope electrospun from WSCA on PU sheet (a) non-fixed and (b) fixed; 0.81 g/m², (c) non-fixed and (d) fixed; 1.61 g/m², (i) non-fixed and (j) fixed; 3.20 g/m², respectively. Similarly, electrospun

CDA fiber morphology observed under 3D microscope on PU sheet from (e) non-fixed and (f) fixed; 0.81 g/m², (g) non-fixed and (h) fixed; 1.61 g/m², (k) non-fixed and (l) fixed; 3.20 g/m², respectively.

3.2.6.3 Preparation of regenerated cellulose fiber

Saponification process was carried out in 28% ammonia aqueous solution atmosphere with four entries in oven and at room temperature in different condition as shown in table **Table 3-1**. Out of four entries, for WSCA entry no 2 and 4 (**Figure 3-15**) and for CDA entry no 1, 2 and 4 (**Figure 3-16**) saponification were succeeded, for better saponification, entry no 2 were used in both CAs saponification. In section 4.2.5 saponification process conditions were shown in **Table 3-1**.

Table 3-1 Condition variation:

Entry	Temperature (°C)	Volume of aq. NH ₃ sol. (mL) used	Time (days)
1	r.t. ^{a)}	25	7
2	r.t.	50	7
3	60 ^{b)}	50	7
4	60	50	3

^{a)} done at a laboratory bench, ^{b)} done in an oven

In oven condition, most of the case PU sheet morphology was almost changed at 60 °C for 3 days as shown in **Figure 3-13**. Whereas, PU sheet morphology was not changed in room temperature condition on laboratory bench at even under 7 days.



Figure 3-13 PU sheet morphology in oven under 3 days at 60 °C.

3.7 Result and discussion

3.7.1 Electrospinning of WSCA on PU sheet with different amount fibers

This experiment was carried out in several times for accurate amount of electrospun fibers deposition on PU sheet. As describe in section 3.2.2.1, polymer solution was poured into a glass syringe about (0.5 mL, 1.0 mL and 2.0 mL) for the preparation of about 0.81 g/m², 1.61 g/m² and 3.20 g/m² electrospun fiber on PU sheet, respectively. All poured polymer solution (in syringe) was electrospinning on PU sheet as described in section 3.2.4. Finally, the fibers deposition amount on PU sheet was successfully completed as shown in **Table 3-2** for WSCA fibers. In **Table 3-2**, all non-

fixed and fixed WSCA fiber amount was summarized on PU sheet. From the both summarized tables, it was clear that fiber amount depends on the amount of polymer solution completely spray.

Table 3-2 Non-fixed and fixed WSCA fiber amount on PU sheet

Sample	Strip number	Wt. of PU sheet after vacco drying overnight (60 ⁰ C)			Wt. of fiber on PU sheet (g)	Wt. of fiber (g/m ²)	Target: 50 mg, 100 mg and 200 mg on A4 sheet
WSCA: 11%		Before spinning (g)	Amount of solution spray about (mL)	After spinning (g)			
50 mg (non-fixed)							
	44	2.4952	0.5	2.5045	0.0093	0.81	0.08 % less
	45	2.5002	0.5	2.5049	0.0092	0.80	0.01 % less
100 mg (non-fixed)							
	46	2.5053	1.0	2.5238	0.0185	1.61	0.08 % more
	47	2.4951	1.0	2.5135	0.0184	1.60	0.01 % less
200 mg (non-fixed)							
	19	2.5071	2.0	2.5442	0.0371	3.20	0.2% more
	20	2.5159	2.0	2.5529	0.0370	3.20	0.2% more
50 mg (fixed)							
	48	2.4975	0.5	2.5070	0.0094	0.82	0.26 % more
	49	2.4975	0.5	2.5070	0.0093	0.82	0.26 % more
100 mg (fixed)							
	43	2.4985	1.0	2.5172	0.0187	1.62	0.25 % more
	50	2.5094	1.0	2.5279	0.0185	1.61	0.08 % more
200 mg (fixed)							
	15	2.5083	2.0	2.5455	0.0372	3.20	0.30% more
	16	2.5117	2.0	2.5488	0.0371	3.20	0.2% more
Area of PU sheet= length 30.30 cm ×width 3.97 cm=114.837 cm ²							

3.7.2 Electrospinning of CDA on PU sheet with different amount fibers

As describe in the section of 3.2.2.1.2, fiber deposition amount on PU sheet depend on the amount polymer solutions spraying. The deposition amount of fibers was increased when polymer solution spraying amount was increased. On the other hand, homogenous fiber deposition was controlled on non-conductive PU sheet during spinning using anti-static agent and at the same time voltage difference was reduced between collector drum (non-conductive PU sheet) and needle tip. As a result, homogenous fiber deposition on PU sheet and fiber fixation with PU sheet was achieved. The result of non-fixed and fixed CDA fiber deposition amount on PU sheet was presented in the **Table 3-3**.

Table 3-3 Non-fixed and fixed CDA fiber amount on PU sheet

Sample	Strip number	Wt. of PU sheet after vacco drying overnight (60 °C)		Wt. of fiber on PU sheet (g)	Wt. of fiber (g/m ²)	Target:
		Before spinning (g)	Amount of solution spray about (mL)			
CDA: 9 %						
	50 mg (non-fixed)					
	51	2.5011	0.5	2.5106	0.0095	0.82
	52	2.5153	0.5	2.5248	0.0095	0.82
100 mg (non-fixed)	53	2.4862	1.0	2.5047	0.0185	1.61
	54	2.5093	1.0	2.5276	0.0183	1.60
	200 mg (non-fixed)					
	21	2.5396	2.0	2.5768	0.0372	3.20
	22	2.5459	2.0	2.5830	0.0371	32.0
50 mg (fixed)	55	2.5004	0.5	2.5098	0.0094	0.82
	56	2.5065	0.5	2.5158	0.0093	0.81
100 mg (fixed)	57	2.4981	1.0	2.5165	0.0184	1.60
	58	2.5003	1.0	2.5189	0.0186	1.62
200 mg (fixed)	23	2.5558	2.0	2.5931	0.0373	3.24
	24	2.5023	2.0	2.5394	0.0371	3.23
Area of PU sheet= length 30.30 cm ×width 3.97 cm=114.837 cm ²						0.4% more
						0.2% more

3.7.3 Fiber fixation with PU sheet

From the section of 3.2.6.1, fiber fixation process depends on the appropriate solvent selection which can be protected the fiber morphology and also some part fused with the PU sheet [Figure 3-11 (a) and (c)]. In this study, poorer diluted solvent could be protected fiber morphology and at the same time electrospun fibers can be able to fuse with PU sheet. As a result, fibers were tightly adhered with porous PU sheet as shown in **Figure 3-14**.

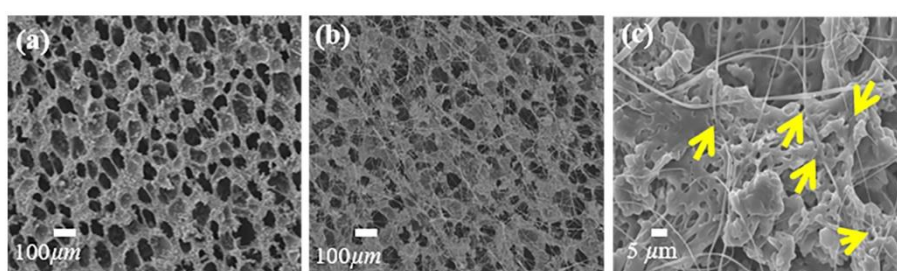


Figure 3-14 SEM images of PU sheet before spinning (a), after spinning (b) and after fixation (c). An arrow shows fused part of CA fibers and PU sheet).

3.7.4 Regenerated cellulose fiber from CAs (WSCA and CDA) characterized through FTIR spectra by saponification.

In the condition variation, entry 2 and 4 shows successful saponification of CAs (WSCA and CDA). For better saponification, I selected the entry condition 2 for WSCA to regenerated cellulose fiber because it was successfully achieved in the room condition with same amount of 28% ammonia aqueous atmosphere.

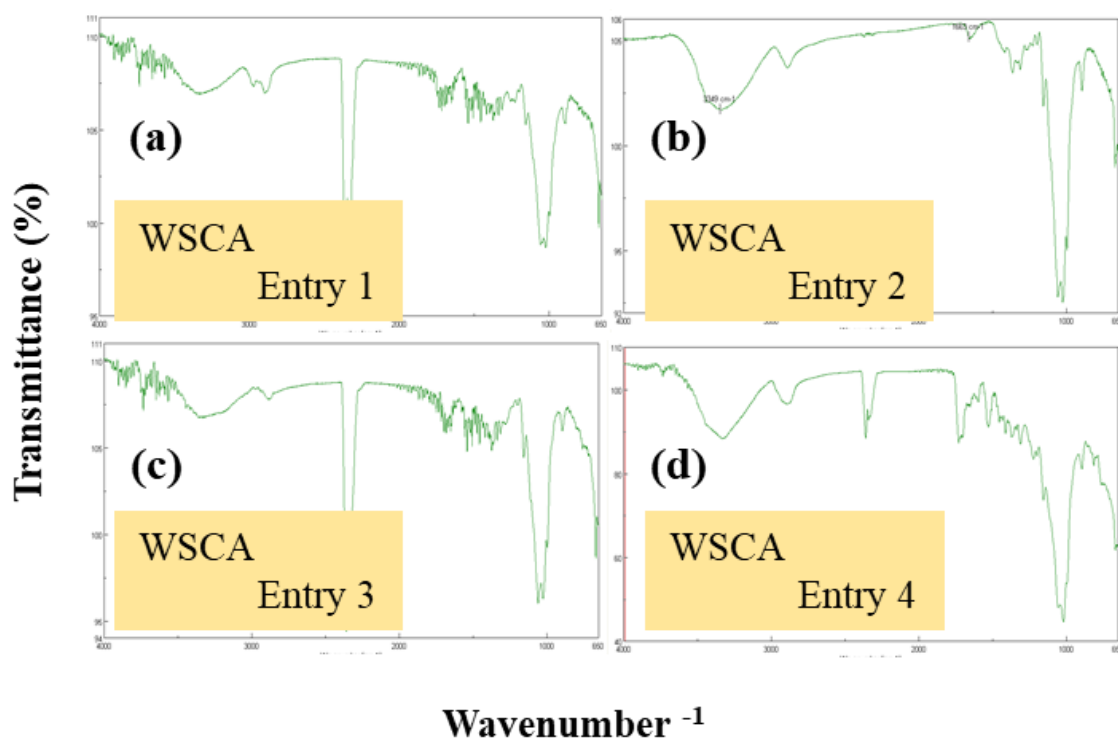


Figure 3-15 FTIR (ATR) spectra of WSCA with different entries (a) entry 1, (b) entry 2, (c) entry 3 and (d) entry 4.

In case of CDA, similarly, I selected the entry condition 2 because, entry no 2 shows comparatively better FTIR spectrum of regenerated cellulose fiber from CDA. Therefore, entry condition no 2 was chosen for better saponification of CDA fibers.

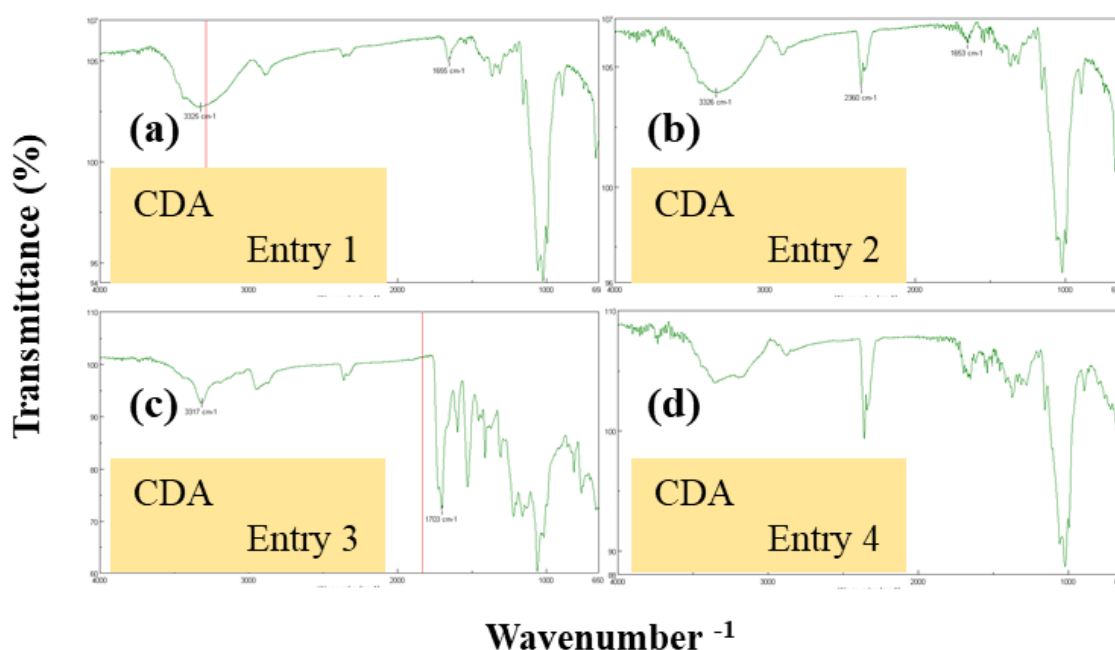


Figure 3-16 FTIR (ATR) spectra of CDA with different entries (a) entry 1, (b) entry 2, (c) entry 3 and (d) entry 4.

Finally, all of the experiments were followed according to the entry condition no 2 for preparation of all regenerated sample's through saponification process. At the final step, all non-saponified and saponified (regenerated) samples were subjected to tribology measurement.

CA was saponified with a vapor of 28% NH_3 aqueous solution to produce regenerated cellulose ([Takahashi et al.2013](#)). The changes in the chemical structure of the CA fibers upon saponification were analyzed by using an attenuated total reflection-Fourier transform Infra-Red spectroscopy (ATR-FTIR). Since PU sheet, itself carries carbonyl groups, the carbonyl band assigned to PU and CA could not be distinguished. Therefore, completion of saponification was monitored by ATR-FTIR, using WSCA and CDA electrospun fibers deposited on aluminum foil.

The peak at around 985cm^{-1} similar in all samples is due to C–H deformation vibrations and C–C vibration in the common aromatic ring region to all cellulose

derivatives. The removal of the acetyl groups from cellulose acetate by saponification is represented by the disappearance of the corresponding peak at $1,745\text{ cm}^{-1}$. The increase in peak strength at around $3,500\text{ cm}^{-1}$ in the regenerated cellulose is attributed to the increase in O–H groups.

In **Figure 3-17**, an ester carbonyl band at 1745 cm^{-1} was clearly observed in the spectra of WSCA and CDA electrospun fibers. The carbonyl band disappeared upon the saponification for 7 d, indicating that both CAs were converted completely to regenerated cellulose. This result was also strongly supported of the filter paper spectra as shown in **Figure 3-17 (f)**.

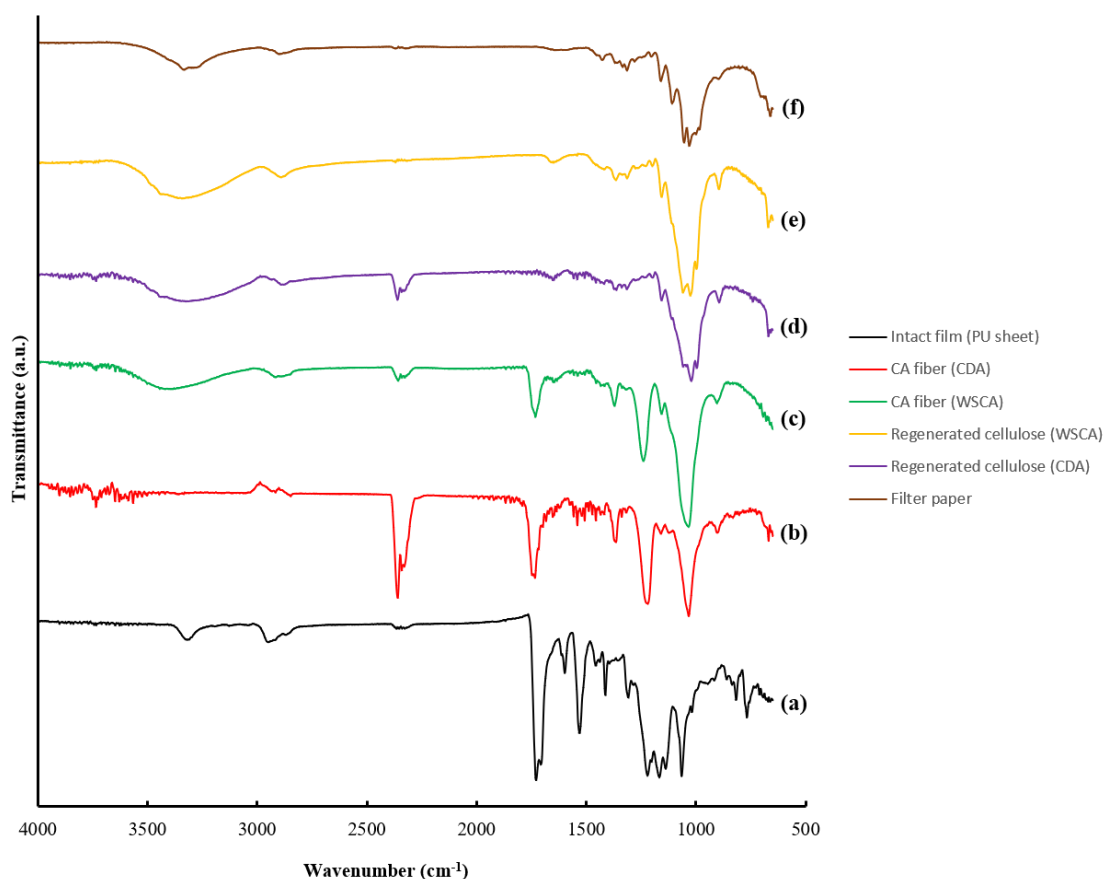


Figure 3-17 ATR-FTIR spectra of PU sheet (a), CDA fibers (b), WSCA fibers (c), saponified CDA fibers (d), saponified WSCA fibers (e) and Filter paper (f).

3.7.5 Regenerated cellulose fiber from CAs (WSCA and CDA) characterized through X-ray diffraction pattern by saponification

For more clarification, the X-ray diffraction pattern was carried out for their crystallinity measurement. X-ray diffraction (XRD) of electrospun CA fibers before and after saponification was measured to elucidate crystalline structure (**Figure 3-18**). Broad peaks at less than 10° and at around 20° were observed in unsaponified WSCA and CDA electrospun fibers [**Figure 3-18 (a) and (b)**], indicating these fibers were amorphous. Saponified CDA fibers showed sharp peaks at $2\theta = 11.6^\circ$, 20.1° , and 21.2° , although each intensity was not so high, suggesting a crystalline structure of cellulose II polymorph [**Figure 3-18 (c)**]. However, saponified WSCA fibers showed peaks at $2\theta = 11.9^\circ$ and 20.0° , where two peaks at 20.1° and 21.3° might be overlapped [**Figure 3-18 (d)**]. This observation suggested that CDA gave the regenerated cellulose with higher crystallinity. Thus, this saponification with NH_3 vapor brought about not only deacetylation but also crystallization.

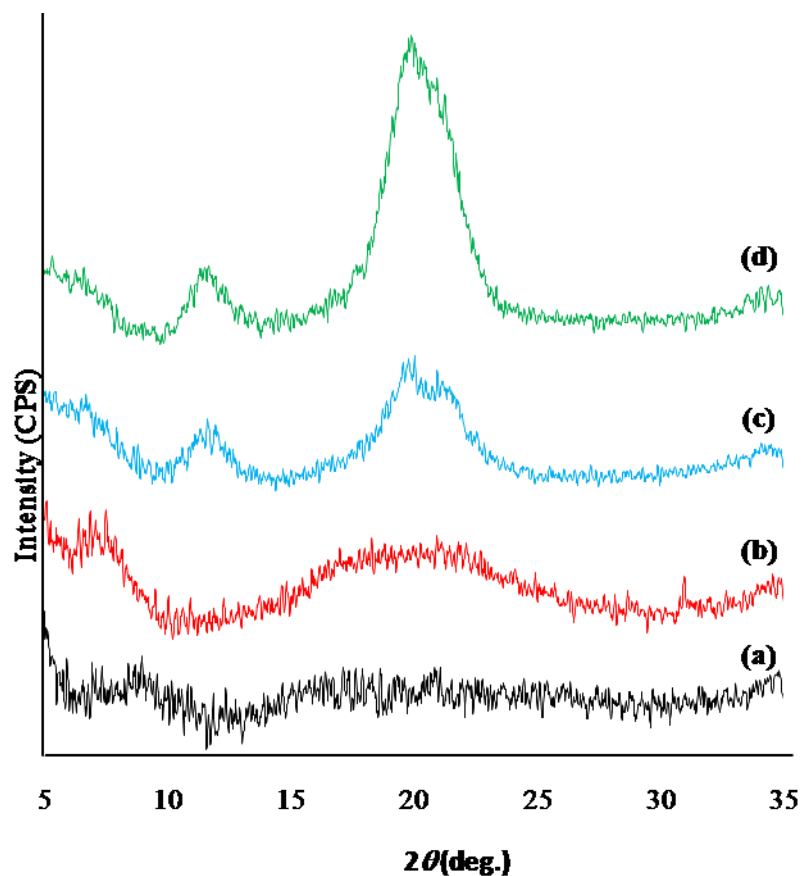


Figure 3-18 X-ray diffractograms of WSCA fibers (a), CDA fibers (b), regenerated cellulose from CDA fibers (c) and regenerated cellulose from WSCA fibers (d).

All saponified and non-saponified samples are subjected for tribology measurement. Tribology measurement process was details describe in the **Chapter 4**.

Chapter 4 Evaluation of surface change of non-saponified and saponified electrospun fibers coated PU sheet through Tribology measurement

4.1 Introduction

When two surface sliding against each other with their in-contacting point by the dissipative force is called friction, which acts to resist the relative motion of the two objects. It is an important physical and mechanical parameter that control the contacting materials motion systems. There are several factors that influence the friction during sliding of the objects each other including normal load, temperature, relative humidity, working conditions and relative surface motion, surface roughness of the rubbing surface, types of materials, etc. Friction forces are mainly classified into two categories: static friction force and kinetic friction force. When the mass of the object is not moving by applying external force, its result is static friction force, which normally express in μ_s . On the other hand, by increasing the applied force on the mass of the object, the object is started to move, its experience is kinetic friction force, which is express in μ_k . The surface topography of the contacting materials is one of the key factors that affect the coefficient of friction (COF) and surface formation during sliding. Many researchers have been investigated and reported about the surface topography of sliding two objects and at the same time surface roughness of materials using different loading condition, to determine the surface smoothness through friction coefficient measurement. Therefore, the role of surface texture and roughness was monitored through Tribogear instrument over on the synthetic and bio-based microfiber coated synthetic surface. Thus, it can be applied on different surface such as bio-based, polymeric and/or reinforcing materials. Electrospun nanofiber and/or microfiber-based

materials are typically susceptible to operate even under conditions of gentle handling. This is the main subject for the post-operative processing as well as the end use of the material. Finally, it could be a critical limitation to their service lifetime. To verify this behavior, the friction coefficient was measured using a standardized tribogear instrument (HHS3000: Shinto Science Co., Ltd, Tokyo, Japan) on electrospun fiber coated PU sheet.

Tribology test was carried out to evaluate the change in physical property of PU sheets upon the electrospun CA fibers deposition and their saponification. Also, to evaluate the surface roughness of electrospun CA fiber-coated and regenerated cellulose fiber coated PU sheet to determine the friction coefficient compare to intact PU sheet to obtained smooth surface for polishing of compact disk and hard disk.

Finally, the goal of this chapter was to investigate the influence of different the applied load on different surface such as on intact PU sheet, CA fiber coated PU sheet, regenerated cellulose fiber coated PU sheet. Also, different amount of non-fixed CA fiber deposited PU sheet and different amount of fixed CA fiber deposited PU sheet against the sensor of aluminum ball.

4.2 Experimental

4.2.1 Materials

Stainless steel plate for tribology measurement was purchased from Yamamoto-MS Co., Ltd. (Tokyo, Japan). Forcep, scale, blade, double side tape etc were purchased from domestic market. Ethanol was purchased from Wako chemical company Ltd. Japan.

4.2.2 Sample preparation for friction coefficient measurement using Tribogear instrument.

As describe in **chapter 3**, (section 3.2.5.1) non-saponified (non-fixed and fixed) and saponified (non-fixed and fixed) samples were used for tribology measurement. The CA fiber-coated film with the fiber amounts of 0.81, 1.61 and 3.20 g/m² was cut into pieces (about 6× 3.8 cm²), and the resultant film was attached as a specimen with double-sided tape on aluminum plate. Finally, it was placed on sample holder of tribogear instrument's (HHS3000: Shinto Science Co., Ltd, Tokyo, Japan) for sliding the probe with aluminum ball as sensor. The aluminum ball is the sensor, which is rubbing on the sample surface of both samples (WSCA and CDA) electrospun CA fiber-coated PU sheet (non-saponified and saponified samples) for friction coefficient measurement. Same measurement procedure was followed in case of intact film as a control sample. During measurement, an aluminum ball (sensor) was kept moving on the specimen under different loadings. The Tripology test conditions were as follows: working distance, 30 mm; scan rate, 2 mm/sec; reciprocation times, 10; loadings, 50, 100 and 150 g. All samples were measured separately with different loading condition and different reciprocation times. The friction coefficients were calculated from measured of friction forces and the loading weights.

4.2.3 Processing of tribological raw data

After the Tribology or friction coefficient measurement, I collect the data grid folder from tribogear instrument. The friction coefficient was calculated from these raw data grid as follows:

1. All raw data grid first of all, I converted the unit of time, milli second (ms) to second (s), and the unit of friction force, milli volt (mV) to Neuton [N],

respectively. The equation of $F(N) = \frac{A(mV)}{252.9}$, where F is friction force, and A is output value of measured voltage.

2. These converted values of Force [N] of all reciprocation time (RT) were selected for total average value. This total average value was deducted from the original raw data line for new data line. These data line is modifying average data line. These modify data line was used for friction profile preparation. These modify data line also can be detected the zero point of each profile for each RT.
3. Then I selected the Force [N] data in accordance with the highest value of initial two seconds. And then, I calculated the average of each selected range. In one second the tribogear machine can be measured five points. Initial high point value (in two second) of each peak or reciprocation time (RT) was selected for static friction measurement. And rest of the data range average of a peak (RT) was calculated for kinetic friction measurement.
4. The kinetic average was transferred to another excel sheet for again average. This average was added to the original selected data line.
5. After adding the average, this data line is modified data grid. Finally, I prepared the friction profile by using the modify data grid. The static and kinetic friction was measured by using modify average.

4.3 Result and discussion

4.3.1 Friction coefficient measurement over WSCA and CDA fiber deposited PU sheet

Tribology tests were performed to evaluate the changes in the physical properties of the PU sheets upon electrospun fiber deposition and saponification. The

amounts of the WSCA and CDA electrospun fibers deposited on the PU sheets corresponded to 0.81, 1.61, and 3.20 g/m². All of the amounts WSCA and CDA electrospun fibers had been deposited on PU sheets as fixed and non-fixed during spinning. The tribology tests were evaluated under the loadings condition of 50, 100 and 150 gf. Theoretically, friction coefficient is a constant value and independent of the loadings. However, friction coefficients of non-saponified and saponified WSCA and CDA fibers-coated PU sheets were decreased with increasing the amount of deposited fibers (**Figure 4-1**). This result indicates that the surface of PU sheets become smoother than that of the intact PU sheets due to the CA fiber deposition over PU sheet. The friction coefficient of porous PU sheets was high, probably due to a rough surface. When CA fibers were deposited on the PU sheet, some pores (concave-convex) were partially covered, and the surface became flat, leading to a decrease in friction coefficient. On the other hand, elastic property of cellulose is higher than that of plastic. Therefore, deformation of PU sheet might be protected by CA and cellulose fibers upon loads. As a result, smooth surface was achieved. The decrement of friction coefficient was related to the amount of deposited fibers. Moreover, stiffness of WSCA and CDA electrospun fibers might affect to keep flatness of that surface for a long time.

The friction coefficients of saponified CDA fibers deposited on PU sheets at any deposition amounts were slightly higher than those of non-saponified ones, but it was always lower than that of intact PU sheet itself. This phenomenon was explained by the change in the CDA fiber structure from amorphous state before saponification to crystalline state after saponification. The deposited crystalline fibers might have high Young's modulus or high stiffness that directly affected the friction coefficient. In the case of saponified WSCA fibers deposited on PU sheets at 0.81 and 1.61 g/m², the friction coefficient had a similar trend to that of saponified CDA fiber, while the

friction coefficient of saponified WSCA fibers at 3.20 g/m² was lower than that of non-saponified ones and were the lowest among samples.

Static (μ_s) and kinetic (μ_k) friction coefficients profile on intact film (PU sheets), WSCA fibers deposited PU sheets and saponified WSCA fibers deposited PU sheet [(a)-(c)]; intact film (PU sheets), CDA fibers deposited PU sheets and saponified CDA fibers deposited PU sheets [(d)-(f)], at the fiber amount of 0.81 g/m² (a) and (d), 1.61 g/m² (b) and (e) and 3.20 g/m² (c) and (f), where the loading condition was **shown** 50 gf in **Figure 4-1**, 100 gf in **Figure 4-2** and 150 gf in **Figure 4-3**, respectively.

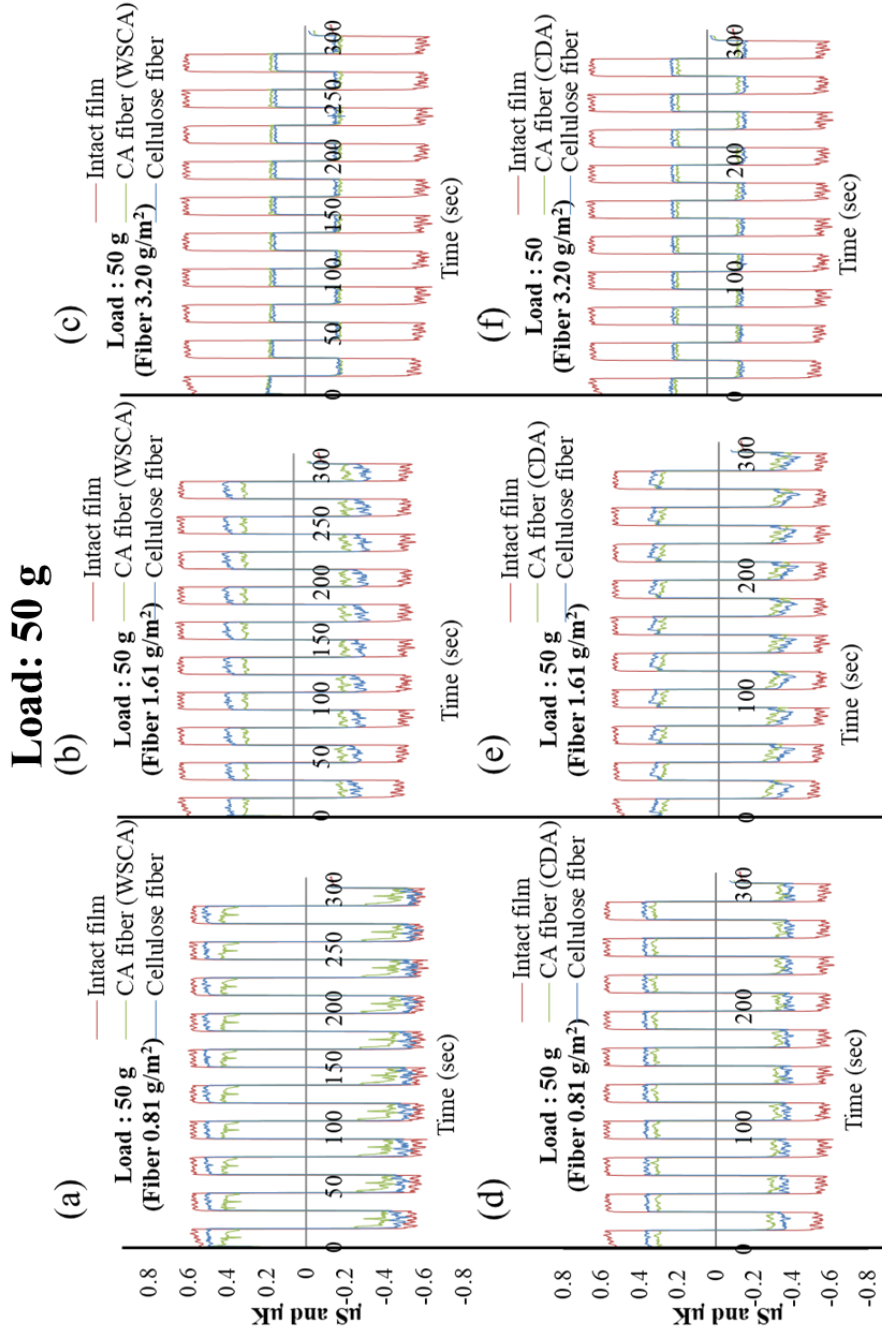


Fig.4-1 Friction coefficient profile of static (μ_s) and kinetic (μ_k) friction coefficients of PU sheets (red line), WSCA fibers (green line) and cellulose fiber [(blue line), (saponified WSCA)] fibers deposited on PU sheets [(a)-(c)] and PU sheets [(d)-(f)], at the fiber amount of 0.81 g/m² (a) and (d), 1.61 g/m² (b) and (e) and 3.20 g/m² (c) and (f), respectively where the loading condition was 50 gf. The friction coefficients are determined over periods of stationary sliding between the directional changes.

Load: 100 g

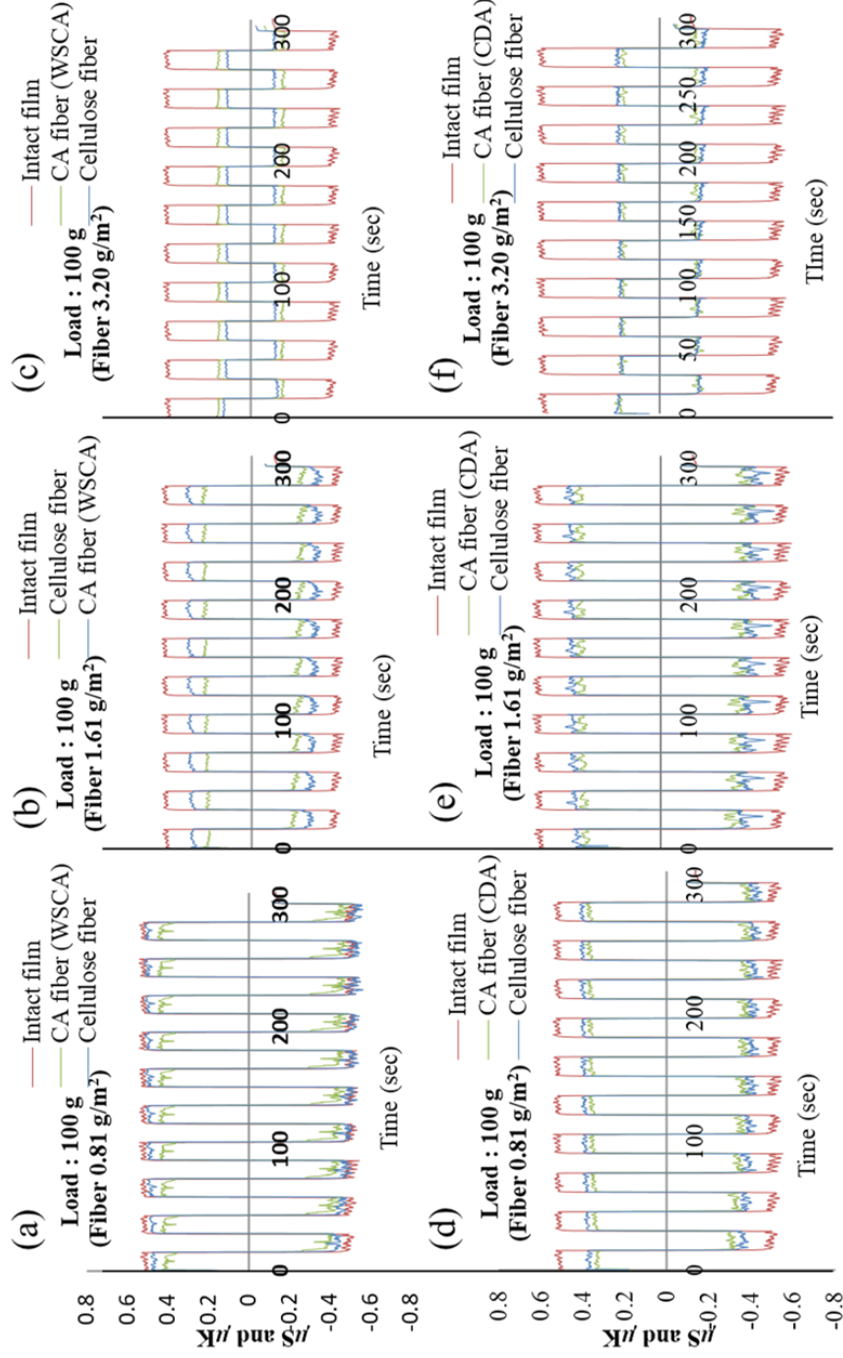


Fig.4-2 Friction coefficient profile of static (μ_s) and kinetic (μ_k) friction coefficients of PU sheets (red line), WSCA fibers (green line) and cellulose fiber [(blue line), (saponified WSCA)] fibers deposited on PU sheets [(a)-(c)] and PU sheets (red line), CDA fibers and cellulose fiber [(blue line), (saponified WSCA)] fibers deposited on PU sheets [(d)-(f)], at the fiber amount of 0.81 g/m² (a) and (d), 1.61 g/m² (b) and (e) and 3.20 g/m² (c) and (f), respectively where the loading condition was 100 gf. The friction coefficients are determined over periods of stationary sliding between the directional changes.

Load: 150 g

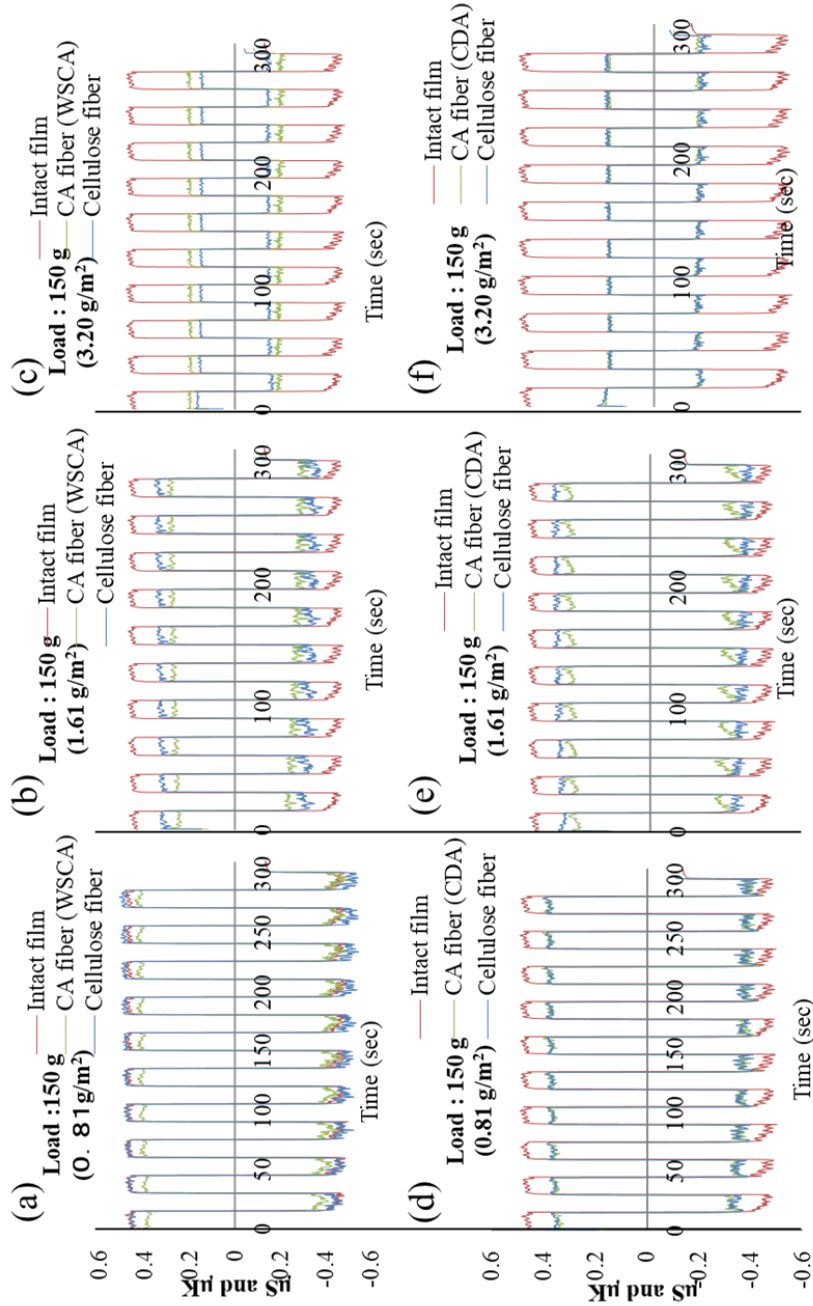


Fig.4.3 Friction coefficient profile of static (μ_s) and kinetic (μ_k) friction coefficients of PU sheets (red line), WSCA fibers (green line) and cellulose fiber [(blue line), (saponified WSCA)] fibers deposited on PU sheets [(a)-(c)] and PU sheets (red line), CDA fibers and cellulose fiber [(blue line), (saponified WSCA)] fibers deposited on PU sheets [(d)-(f)], at the fiber amount of 0.81 g/m² (a) and (d), 1.61 g/m² (b) and (e) and 3.20 g/m² (c) and (f), respectively where the loading condition was 150 gf. The friction coefficients are determined over periods of stationary sliding between the directional changes.

Although the reason for the lowest coefficient is unclear, the thickness or the diameter of the electrospun fibers may affect the friction coefficient. The average diameter of $1.16 \pm 0.31 \mu\text{m}$ of the saponified WSCA electrospun fibers was smaller than that of CDA fibers $1.73 \pm 0.23 \mu\text{m}$. When a significantly higher amount of fine CA fibers was deposited on the PU sheets, the surface pores of the PU sheet was

considered to be densely covered with the thin fibers to give flatter surface and lower resistance to the friction against an aluminum ball as a probe of this tribology measurement. The smaller surface roughness of the WSCA fibers (3.20 g/m²)-deposited PU sheet was confirmed by 3-D laser microscopic observation, according to ISO 4287: 1997 as shown in **Table 4-4**.

Table 4-4 Relationship between fiber diameter and surface roughness

Saponified fibers	Average diameter (μm)	Surface roughness (μm)		
		Ra	Rp + Rv	Rz
WSCA at 11% (w/w)	1.16	7.40	129	129
CDA at 9% (w/w)	1.73	7.26	245	237

Ra: Arithmetic average roughness

Rp: Maximum peak height in the assessed profile obtained from 3-D microscopic observation

Rv: Maximum depth in the assessed profile obtained from 3-D microscopic observation

Rz: 10-point average roughness

The detailed explanation is available at <http://www.iso.org/obp/ui/#iso:std:iso:4287:ed-1:vl:fr>

Ra value of both saponified fibers were almost identical, while Rp + Rv and Rz of saponified WSCA fibers were much smaller than those of CDA fibers. Therefore, smaller fiber diameter gives smaller roughness or flatter surface. Thus, the surface physical property of PU sheets was found to be dramatically altered by the deposition of WSCA and CDA electrospun fibers and their saponification.

The friction coefficients are determined over periods of stationary sliding between the directional changes. All tribological data of static (μ_s) and kinetic (μ_k) friction coefficients with different loading conditions were calculated and compiled in **Table 4-**

Table 1. Friction coefficient of intact PU sheet, CDA and WSCA electrospun fibers-deposited on PU sheet, and their saponified fibers-deposited PU sheet with varying amounts of deposited fibers under different loads (50, 100 and 150 gf).

Friction coefficient	PU sheet	Fiber amount 0.81 mg /m ²						Fiber amount 1.61 mg /m ²						Fiber amount 3.20 mg /m ²												
		WSCA			CDA			WSCA			CDA			WSCA			CDA									
		Before ^a	SD	After ^b	Before ^a	SD	After ^b	Before ^a	SD	After ^b	Before ^a	SD	After ^b	Before ^a	SD	After ^b	Before ^a	SD	After ^b							
		Load : 50 gf																								
μ_s	0.560	0.02	0.418	0.02	0.515	0.02	0.322	0.01	0.387	0.01	0.269	0.01	0.334	0.01	0.323	0.01	0.355	0.01	0.172	0.01	0.155	0.01	0.154	0.01	0.174	0.01
μ_k	0.564	0.01	0.411	0.01	0.502	0.01	0.315	0.01	0.367	0.01	0.248	0.01	0.378	0.01	0.315	0.01	0.357	0.01	0.166	0.01	0.149	0.01	0.149	0.01	0.170	0.01
Load : 100 gf																										
μ_s	0.507	0.01	0.430	0.02	0.499	0.02	0.370	0.02	0.409	0.02	0.290	0.01	0.365	0.01	0.349	0.02	0.391	0.01	0.205	0.01	0.154	0.01	0.164	0.01	0.181	0.01
μ_k	0.509	0.01	0.423	0.01	0.489	0.02	0.352	0.02	0.389	0.01	0.275	0.01	0.356	0.01	0.332	0.01	0.371	0.01	0.195	0.01	0.147	0.01	0.159	0.01	0.176	0.01
Load : 150 gf																										
μ_s	0.444	0.01	0.409	0.02	0.483	0.02	0.395	0.02	0.394	0.01	0.301	0.02	0.338	0.01	0.342	0.01	0.380	0.01	0.206	0.01	0.157	0.01	0.163	0.01	0.168	0.01
μ_k	0.459	0.01	0.409	0.02	0.475	0.02	0.365	0.02	0.365	0.01	0.279	0.02	0.338	0.01	0.316	0.01	0.366	0.01	0.202	0.01	0.152	0.01	0.160	0.01	0.163	0.01

μ_s and μ_k are static friction coefficient and kinetic friction coefficient, respectively.

^a Before saponification. ^b After saponification.

SD: Standard deviation

Moving speed of aluminum ball: 2 mm/sec, Distance: 30 mm, Reciprocation: 10 times

Chapter 5 General conclusion

Recently, cellulose has drawn much attention to many researchers and scientist due to its attractive properties such as blending capability of cellulose with other polymers, biocompatibility and self-utilizations in different fields like as natural cellulose. This is because that around 180 billion tons of waste biomass produces in every year from natural resources. Therefore, huge amount of effective unused major biomass component is target to the scientific community to collect bio-based polymer cellulose and lignin from the plant kingdom and sometime in lower invertebrate (tunicate) which is mostly abundant and renewable resources after its intended utilization on earth. For the sustainable production, based on renewable woody biomass, cellulose utilization is one of the key factors to fabricate bio-based materials using new and innovative technology. Thus, many companies and industries are trying to produce different bio-based products according to consumers demands using abundant, renewable and sustainable resources. This is because, the products made from cellulose which is non-petroleum based and environmentally friendly with zero emission, reduced animal/human health and safety risks to the society. There are many applications of cellulosic (bio-based) products, produced through electrospinning process, such as separation membrane, affinity membrane, air filter, medical application (drug release, scaffold tissue engineering, wound healing), etc. However, all most all electrospun materials were produced on aluminum foil as a collector substrate material due to its electrical conductivity. It is also intensively investigated on micro pattern template assist and on nylon mesh based over synthetic polymer. However, these are not necessarily considered to be surface modification with electrospun CA fiber over PU

sheet (plastic surface) which is electrically insulator to alter the physical properties of PU sheet (concave-convex). The PU sheet is industrially produced for polishing pad by Fujibo Ehinbo, Co. Ltd., Japan. This artificially produce PU sheet have big pores to change the big pore into small pores through electrospinning with cellulose submicron fibers for getting smooth surface as a polishing material such as compact disk (CD) and hard disk (HD). As a result, development of bio-based materials production from cellulose is an important research tropic to promote the cellulose utilization. From this viewpoint, I prepared CA sub-micron electrospun fiber-deposited synthetic surface modified PU sheet for use as a bio-based polishing material to getting smooth surface.

In this study, modification of surface physical property of PU sheet was attempted by direct electrospinning of CAs (WSCA and CDA) solutions. Fine electrospun fibers with diameters of 1.20 μm and 1.69 μm were obtained from 11wt.% of WSCA in 40 wt.% aqueous ethanol solution and 9 wt.% of CDA in 90 wt.% aqueous acetone solutions, respectively. Direct electrospinning of both CA fibers on non-electroconductive PU sheets was successfully carried out by spraying an anti-static agent on PU sheet during spinning to remove the static charge. This method of spraying an anti-static agent enabled direct electrospinning of CA on any synthetic polymer sheet, such as polyethylene and poly(methyl methacrylate).

Although the deposited fibers on PU sheet were easily peeled off from PU sheet by finger rubbing, the fiber was tightly fixed on the sheet by dragging the fiber-deposited PU sheets in the mist comprised of a mixed solvent of DMF/EtOH (1/1) followed by partly fusion of the fibers with the surface of PU sheet. The WSCA and CDA electrospun fibers were saponified with NH_3 vapor to yield regenerated cellulose fibers with crystalline structure of cellulose II polymorph. In tribology test, the friction coefficients of electrospun CA fibers-deposited PU sheet were decreased with an

increase in the amount of CA fibers deposition. Moreover, the friction coefficients of the sheet were slightly increased by saponification, except for WSCA fibers-deposited PU sheet at 3.20 g/m². Thus, surface physical property of porous PU sheets was successfully altered by direct electrospinning of CAs and their saponification. I am convinced that this research achievements and findings will contribute not only to the requirement of modern conscious society for a new and innovative technology-based product (cellulose) application, but also to the development of cellulose utilization. However, study on cellulose in terms of structure and its application is still promising and is expected to be further develop in different fields.

Reference

- Abdul Latif, N. I. S., Ong, M. Y., and Nomanbhay, S. (2019)** Hydrothermal liquefaction of Malaysia's algal biomass for high-quality bio-oil production. *Eng. Life Sci.*, 19: 246 – 269.
<https://doi.org/10.1002/elsc.201800144>
- Abe, K. and Yano, H. (2012)** Cellulose nanofiber-based hydrogels with high mechanical strength. *Cellulose*, 19:1907–1912.
<https://doi.org/10.1007/s10570-012-9784-3>
- Adepu, S., Gaydhane, M. K., Kakunuri, M., Sharma, C. S., Khandelwal, M., and Eichhorn, S. J. (2017)** Effect of micropatterning induced surface hydrophobicity on drug release from electrospun cellulose acetate nanofibers. *Appl. Surf. Sci.*, 426: 755–762.
<https://doi.org/10.1016/j.apsusc.2017.07.197>
- Al-Battashi, H. S., Annamalai, N., Sivakumar, N., Al-Bahry, S., Tripathi, B. N., Nguyen, Q. D., and Gupta, V. K. (2019)** Lignocellulosic biomass (LCB): a potential alternative biorefinery feedstock for polyhydroxyalkanoates production. *Rev. Environ. Sci. Bio.* 18: 183–205.
<https://doi.org/10.1007/s11157-018-09488-4>
- Amiraliyan, N., Nouri, M., and Kish, M. H. (2009)** Electrospinning of silk nanofibers. I. An investigation of nanofiber morphology and process optimization using response surface methodology. *Fibers and Polymers*, 10: 167–176.

<https://doi.org/10.1007/s12221-009-0167-9>

Amna, T., Yang, J., Ryu, K. S., and Hwang, I. H. (2014) Electrospun antimicrobial hybrid mats: Innovative packaging material for meat and meat-products. *Journal of Food Sci. Technol.*, 52: 4600–4606.

<https://doi.org/10.1007/s13197-014-1508-2>

Arslan, O., Aytac, Z., and Uyar, T. (2016) Superhydrophobic, Hybrid, Electrospun Cellulose Acetate Nanofibrous Mats for Oil/Water Separation by Tailored Surface Modification. *ACS Appl. Mater. Interfaces*, 8: 19747–19754.

<https://doi.org/10.1021/acsami.6b05429>

Ávila Ramírez, J. A., Gómez Hoyos, C., Arroyo, S., Cerrutti, P., and Foresti, M. L. (2016). Acetylation of bacterial cellulose catalyzed by citric acid: Use of reaction conditions for tailoring the esterification extent. *Carbohydr. Polym.*, 153: 686–695.

<https://doi.org/10.1016/j.carbpol.2016.08.009>

Bhardwaj, N., and Kundu, S. C. (2010) Electrospinning: A fascinating fiber fabrication technique. *Biotechnol. Adv.*, 28: 325–347.

<https://doi.org/10.1016/j.biotechadv.2010.01.004>

Britain, G. (1969) Electrically driven jets. *Pro.Roy. Soc. Lond.*, A 313: 453-575.

Budinger, W. D., and Jensen, E.W. (1990) Pad material for grinding, lapping and polishing. U.S. Patent 4,927,432.

Capellán-Pérez, I., Mediavilla, M., de Castro, C., Carpintero, Ó., and Miguel, L. J. (2014) Fossil fuel depletion and socio-economic scenarios: An integrated approach. *Energy*, 77: 641–666.

<https://doi.org/10.1016/j.energy.2014.09.063>

Carrick, C., and Larsson, P. T. (2014) Lightweight, Highly Compressible, Noncrystalline Cellulose Capsules. *Langmuir*, 30: 7635–7644.

<https://doi.org/10.1021/la501118b>

Cazón, P., Vázquez, M., and Velazquez, G. (2018) Composite films of regenerate cellulose with chitosan and polyvinyl alcohol: Evaluation of water adsorption, mechanical and optical properties. *Int. J. Biol. Macromol.*, 117: 235–246.

<https://doi.org/10.1016/j.ijbiomac.2018.05.148>

Chattopadhyay, S., Hatton, T. A., and Rutledge, G. C. (2015) Aerosol filtration using electrospun cellulose acetate fibers. *J. Mater. Sci.*, 51: 204–217.

<https://doi.org/10.1007/s10853-015-9286-4>

Chupin, L., Arnoult, S., Brancourt-Hulmel, M., Lapierre, C., Gineau, E., and Navard, P. (2017) Polyethylene composites made from below-ground miscanthus biomass. *Ind. Crop Prod.*, 109: 523–528.

<https://doi.org/10.1016/j.indcrop.2017.09.007>

- Cremer, L., Gutierrez, J., Martinez, J., Materon, L. A., Gilkerson, R., Xu, F., and Lozano, K. (2018)** Development of antimicrobial chitosan-based nanofiber dressings for wound healing applications. *Nanomed. J.*, 5: 6–14.
<https://doi.org/10.22038/nmj.2018.05.002>
- Cooley, J. F.; Eastman, A. (1902)** Apparatus for electrically dispersing fluids. U.S. Patent 692,631.
- D'Halluin, M., Rull-Barrull, J., Bretel, G., Labrugère, C., Le Grogne, E., and Felpin, F. X. (2017)** Chemically modified cellulose filter paper for heavy metal remediation in water. *ACS Sustainable Chem. Eng.*, 5: 1965–1973.
<https://doi.org/10.1021/acssuschemeng.6b02768>
- Mares, L. (2018)** Method for depositing a layer of polymeric nanofibers prepared by electrostatic spinning of a polymer solution or melt on electrically nonconductive materials, and a multilayer composite thus prepared containing at least one layer of polymeric nanofibers.
The Patent Cooperation Treaty (PCT), International publication number: WO 2018/064992 A1.
- Diddens, I., Murphy, B., Krisch, M., and Müller, M. (2008)** Anisotropic Elastic Properties of Cellulose Measured Using Inelastic X-ray Scattering. *Macromolecules*, 41: 9755–9759.
<https://doi.org/10.1021/ma801796u>
- Ding, B., Wang, M., Wang, X., Yu, J., and Sun, G. (2010)** Electrospun nanomaterials for ultrasensitive sensors Increasing demands for ever more sensitive sensors for global. *Mater. Today*, 13: 16–27.
[https://doi.org/10.1016/S1369-7021\(10\)70200-5](https://doi.org/10.1016/S1369-7021(10)70200-5)
- Eichhorn, S. J., and Davies, G. R. (2006)** Modelling the crystalline deformation of Native and regenerated cellulose. *Cellulose*, 13: 291–307.
<https://doi.org/10.1007/s10570-006-9046-3>
- Faccini, M., Vaquero, C., and Amantia, D. (2012).** Development of Protective Clothing against Nanoparticle Based on Electrospun Nanofibers. *J. Nanomater.*, 2012: 1-9.
<https://doi.org/10.1155/2012/892894>
- Festucci-Buselli, R. A., Otoni, W. C., and Joshi, C. P. (2007)** Structure, organization, and functions of cellulose synthase complexes in higher plants. *Braz. J. Plant Physiol.*, 19: 1–13.
<https://doi.org/10.1590/s1677-04202007000100001>
- Formhals, A. (1934)** Process and apparatus for preparing artificial threads. U.S. Patent 1,975,504.
- Gironi, F., and Piemonte, V. (2011)** Bioplastics and petroleum-based plastics: Strengths and weaknesses. *Energy sources, Part A*, 33: 1949–1959.

<https://doi.org/10.1080/15567030903436830>

- Gong, J., Li, J., and Xu, J. (2017)** Research on cellulose nanocrystals produced from cellulose sources with various polymorphs. *RSC Advances*, 7: 33486–33493.
<https://doi.org/10.1039/c7ra06222b>
- Hardick, O., Dods, S., Stevens, B., and Bracewell, D. G. (2013)** Nanofiber adsorbents for high productivity downstream processing. *Biotechnol. Bioengineer.*, 110: 1119–1128.
<https://doi.org/10.1002/bit.24765>
- Ho, J.-K., Huang, C.-Y., Tsai, M.-Y., and Tsai, C.-C. (2016)** Investigation of Polishing Pads Impregnated with Fe and Al₂O₃ Particles for Single-Crystal Silicon Carbide Wafers. *Appl. Sci.*, 6: 89-96.
<https://doi.org/10.3390/app6030089>
- Hottle, T. A., Bilec, M. M., and Landis, A. E. (2013)** Sustainability assessments of bio-based polymers. *Polym. Degrad. Stabil.*, 98: 1898–1907.
<https://doi.org/10.1016/j.polymdegradstab.2013.06.016>
- Hou, Z., Li, G., Lian, H., and Lin, J. (2012)** One-dimensional luminescent materials derived from the electrospinning process: preparation, characteristics and application. *J. Mater Chem.*, 22: 5254–5276.
<https://doi.org/10.1039/c2jm15638e>
- Huang, Z., Zhang, Y., Kotaki, M., and Ramakrishna, S. (2003)** A review on Polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Sci. Technol.* 63:2223–2253.
[https://doi.org/10.1016/S0266-3538\(03\)00178-7](https://doi.org/10.1016/S0266-3538(03)00178-7)
- Kakunuri, M., Wanasekara, N. D., Sharma, C. S., Khandelwal, M., and Eichhorn, S. J. (2017)** Three-dimensional electrospun micropatterned cellulose acetate nanofiber surfaces with tunable wettability. *J. Appl. Polym. Sci.*, 134: 44709–44715. <https://doi.org/10.1002/app.44709>
- Kim, S. W., Han, S. O., Sim, I. N., Cheon, J. Y., and Park, W. H. (2015)** Fabrication and Characterization of cellulose acetate/montmorillonite composite nanofibers by electrospinning. *J. Nanomater.*, 1 – 8.
<https://doi.org/10.1155/2015/275230>
- Kolpak, F. J., and Blackwell, J. (1976)** Determination of the Structure of Cellulose II. *Macromolecules*, 9: 273–278.
<https://doi.org/10.1021/ma60050a019>
- Kongkhlang, T., Tashiro, K., Kotaki, M., and Chirachanchai, S. (2008)** Electrospinning as a New Technique To Control the Crystal Morphology and Molecular Orientation of Polyoxymethylene Nanofibers. *J. Am. Chem. Soc.*, 130:15460–15466.
<https://doi.org/10.1021/ja804185s>

- Kose, R., Kasai, W., and Kondo, T. (2011)** Switching surface properties of substrates by coating with a cellulose nanofiber having a high adsorbability. *Sen'i Gakkaishi*, 67: 163–168.
<https://doi.org/10.2115/fiber.67.163>
- Kwon, G., Gupta, K. C., Jung, K., and Kang, I. (2017)** Lamination of microfibrillar PLGA fabric by electrospinning a layer of collagen- hydroxyapatite composite nanofibers for bone tissue engineering. *Biomater. Res.*, 1–12.
<https://doi.org/10.1186/s40824-017-0097-3>
- Lee, K. Y., Jeong, L., Kang, Y. O., Lee, S. J., and Park, W. H. (2009)** Electrospinning of polysaccharides for regenerative medicine. *Advanced Drug Delivery Reviews*, 61: 1020–1032.
<https://doi.org/10.1016/j.addr.2009.07.006>
- Lenart, W. R., Jang, K. S., Jordan, A. M., Baer, E., and Korley, L. S. T. J. (2016)** Mechanically tunable dual-component polyolefin fiber mats via two-dimensional multilayer coextrusion. *Polymer*, 103: 328–336.
<https://doi.org/10.1016/j.polymer.2016.09.060>
- Lewandowski, C. M. (2013)** *FAO Statistical Yearbook. World Food and Agriculture. The effects of brief mindfulness intervention on acute pain experience: An examination of individual difference (Vol. 1).*
<https://doi.org/10.1017/CBO9781107415324.004>
- Li, W. J., Laurencin, C. T., Caterson, E. J., Tuan, R. S., and Ko, F. K. (2002)** Electrospun nanofibrous structure: A novel scaffold for tissue engineering. *J Bio Mater Res*, 60: 613–621. Retrieved from
<http://www.scopus.com/inward/record.url?eid=2-s2.0-0037097175&partnerID=40&md5=1f0e8d00c3f1d306e108ac2b09971826>
- Li, W. J., Tuli, R., Okafor, C., Derfoul, A., Danielson, K. G., Hall, D. J., and Tuan, R. S. (2005)** A three-dimensional nanofibrous scaffold for cartilage tissue engineering using human mesenchymal stem cells. *Biomaterials*, 26: 599–609.
<https://doi.org/10.1016/j.biomaterials.2004.03.005>
- Liu, Q., Lu, Y., Aguedo, M., Jacquet, N., Ouyang, C., He, W., ... Richel, A. (2017)** Isolation of High-Purity Cellulose Nanofibers from Wheat Straw through the Combined Environmentally Friendly Methods of Steam Explosion, Microwave-Assisted Hydrolysis, and Microfluidization. *ACS Sustainable Chem. Eng.*, 5: 6183–6191.
<https://doi.org/10.1021/acssuschemeng.7b01108>
- Liu, Y., Zhou, J., Chen, L., Zhang, P., Fu, W., Zhao, H., ... Xie, E. (2015)** Highly Flexible Freestanding Porous Carbon Nanofibers for Electrode Materials of High-Performance All-Carbon Supercapacitors. *ACS Appl. Mater. Interfaces*, 7: 23515–23520.
<https://doi.org/10.1021/acsami.5b06107>

- López-Velázquez, D., Hernández-Sosa, A. R., and Pérez, E. (2015)** Effect of the degree of substitution in the transition temperatures and hydrophobicity of hydroxypropyl cellulose esters. *Carbohydr. Polym.*, 125: 224–231.
<https://doi.org/10.1016/j.carbpol.2014.12.086>
- Lukanina, K. I., Grigoriev, T. E., Krasheninnikov, S. V., Mamagulashvili, V. G., Kamyshinsky, R. A., and Chvalun, S. N. (2018)** Multi-hierarchical tissue-engineering ECM-like scaffolds based on cellulose acetate with collagen and chitosan fillers. *Carbohydr. Polym.*, 191: 119–126.
<https://doi.org/10.1016/j.carbpol.2018.02.061>
- Lyons, J., Li, C., and Ko, F. (2004)** Melt-electrospinning part I : processing parameters and geometric properties. *Polymer*, 45: 7597–7603.
<https://doi.org/10.1016/j.polymer.2004.08.071>
- Marchenko, G. N. (1984)** Crystal structure of cellulose polymorphs by potential energy calculations: 1. Most probable models for mercerized cellulose. *Polymer*, 25: 107–114.
- Marques, A. C., Fuinhas, J. A., and Pereira, D. A. (2018)** Have fossil fuels been substituted by renewables? An empirical assessment for 10 European countries. *Energy Policy*, 116: 257–265.
<https://doi.org/10.1016/j.enpol.2018.02.021>
- Matsuo, M., Sawatari, C., Iwai, Y., and Ozaki, F. (1990)** Effect of Orientation Distribution and Crystallinity on the Measurement by X-ray Diffraction of the Crystal Lattice Moduli of Cellulose I and II. *Macromolecules* 23: 3266–3275.
<https://doi.org/10.1021/ma00215a012>
- Nicosia, A., Keppler, T., Müller, F. A., Vazquez, B., Ravegnani, F., and Monticelli, P. (2016)** Cellulose acetate nanofiber electrospun on nylon substrate as novel composite matrix for efficient, heat-resistant, air filters. *Chem. Eng. Sci.*, 153: 284–294.
<https://doi.org/10.1016/j.ces.2016.07.017>
- Nishino, T., Takano, K., and Nakamae, K. (1995)** Elastic modulus of the crystalline regions of cellulose polymorphs. *J. Polym. Sci. Part B: Polym. Phys.*, 33: 1647–1651.
<https://doi.org/10.1002/polb.1995.090331110>
- Nishiyama, Y., Sugiyama, J., Chanzy, H., Langan, P., V. K. U., Recherches, C. De, ... R, I. (2003)** Crystal Structure and Hydrogen Bonding System in Cellulose I α from Synchrotron X-ray and Neutron Fiber Diffraction. *J Am. Chem.Soc.*, 125: 14300–14306.
<https://doi.org/10.1021/ja037055w>
- Nogi, B. M., Iwamoto, S., and Nakagaito, A. N. (2009)** Optically Transparent Nanofiber Paper. *Adv. Mater.* 21: 1595–1598.
<https://doi.org/10.1002/adma.200803174>

- Norton, C. L., and Mass, B. (1936)** Method of and apparatus for producing fibers or Filamentary material. U.S. Patent 2,048,651.
- Pourali, P., Razavianzadeh, N., Khojasteh, L., and Yahyaei, B. (2018)** Assessment of the cutaneous wound healing efficiency of acidic, neutral and alkaline bacterial cellulose membrane in rat. *J. Mater. Sci.: Mater. Medi.*, 29: 90-99.
<https://doi.org/10.1007/s10856-018-6099-4>
- Rutledge, G. C., and Fridrikh, S. V. (2007)** Formation of fibers by electrospinning. *Advanced Drug Delivery Reviews*, 59: 1384–1391.
<https://doi.org/10.1016/j.addr.2007.04.020>
- Sakakibara, K., Moriki, Y., Yano, H., and Tsujii, Y. (2017)** Strategy for the Improvement of the Mechanical Properties of Cellulose Nanofiber-Reinforced High-Density Polyethylene Nanocomposites Using Diblock Copolymer Dispersants. *ACS Appl. Mater. Interfaces*, 9: 44079–44087.
<https://doi.org/10.1021/acsami.7b13963>
- Sakurada, I., Nukushima, Y. and Ito, T. (1962)** Experimental determination of the Elastic modulus of crystalline regions in oriented polymers. *J. Polym. Sci.*, 57: 651–660.
- Sakurada, I., and Nakama, T. I. K. (1964)** Elastic moduli of crystal lattices of polymers. *Bulletin of the Institute for Chemical Research, Kyoto University* 42(2-3): 77-92.
- Santos, R. P. de O., Rossi, P. F., Ramos, L. A., and Frollini, E. (2018)** Renewable resources and a recycled polymer as raw materials: Mats from electrospinning of lignocellulosic biomass and PET solutions. *Polymers*, 10: 538-553.
<https://doi.org/10.3390/polym10050538>
- Sarko, A., and Mugglilb, R. (1973)** Packing analysis of carbohydrates and polysaccharides. III. *Valonia* cellulose and cellulose II^{la}. *Macromolecules* 7: 486–494.
<https://doi.org/10.1021/ma60040a016>
- Schön, J. (2004)** Coefficient of friction for aluminum in contact with a carbon fiber epoxy composite. *Tribol. Int.*, 37: 395–404.
<https://doi.org/10.1016/j.triboint.2003.11.008>
- Sehaqui, H., Zhou, Q., Ikkala, O., and Berglund, L. A. (2011)** Strong and tough cellulose nanopaper with high specific surface area and porosity. *Biomacromolecules*, 12: 3638–3644.
<https://doi.org/10.1021/bm2008907>
- Shaghaleh, H., Xu, X., and Wang, S. (2018)** Current progress in production of biopolymeric materials based on cellulose, cellulose nanofibers, and cellulose derivatives. *RSC Advances*, 8: 825–842.
<https://doi.org/10.1039/c7ra11157f>

- Sixta, H. (2006)** Kraft pulping kinetics. Handbook of pulp. Vol: 1, ISBN: 3-527-30999-3, WILEY-ECH Verlag and Co.KGaA. Lenzing, Austria.
- Song, Z., Chiang, S. W., Chu, X., Du, H., Li, J., Gan, L., ... Kang, F. (2018)** Effects of solvent on structures and properties of electrospun poly(ethylene oxide) nanofibers. *J. Appl. Polym. Sci.*, 135: 45787–45797.
<https://doi.org/10.1002/app.45787>
- Sridhar, R., Lakshminarayanan, R., Madhaiyan, K., Barathi, V. A., Limh, K. H. C., and Ramakrishna, S. (2015)** Electrosprayed nanoparticles and electrospun nanofibers based on natural materials: Applications in tissue regeneration, drug delivery and pharmaceuticals. *Chem. Soc. Rev.*, 44: 790 – 814.
<https://doi.org/10.1039/c4cs00226a>
- Takahashi, T., Oowaki, M., and Onohara, Y. (2013)** Deodorant performance of titanium dioxide-added acrylic/cellulose diacetate blended fibers. *Textile Research Journal*, 83: 800-812.
<https://doi.org/10.1177/0040517512460295>
- Tarus, B., Fadel, N., Al-Oufy, A., and El-Messiry, M. (2016)** Effect of polymer concentration on the morphology and mechanical characteristics of electrospun cellulose acetate and poly (vinyl chloride) nanofiber mats. *Alexandria Engineering Journal*, 55: 2975–2984.
<https://doi.org/10.1016/j.aej.2016.04.025>
- Taylor, P., and Frey, M. W. (2008)** Electrospinning Cellulose and Cellulose Derivatives. *Polym. Rev.*, 48: 378 – 391.
<https://doi.org/10.1080/15583720802022281>
- Tashiro, K., and Kobayashi, M. (1991)** Theoretical evaluation of three-dimensional elastic constants of native and regenerated celluloses: role of hydrogen bonds. *Polymer*, 32: 1516–1526.
[https://doi.org/10.1016/0032-3861\(91\)90435-L](https://doi.org/10.1016/0032-3861(91)90435-L)
- Vallejos, M. E., Peresin, M. S., and Rojas, O. J. (2012)** All-Cellulose Composite Fibers Obtained by Electrospinning Dispersions of Cellulose Acetate and Cellulose Nanocrystals. *J. Polym. Environ.*, 20: 1075–1083.
<https://doi.org/10.1007/s10924-012-0499-1>
- Vaz, C. M., Tuijl, S. Van, Bouten, C. V. C., and Baaijens, F. P. T. (2005)** Design of scaffolds for blood vessel tissue engineering using a multi-layering electrospinning technique. *Acta Biomaterialia* 1: 575–582.
<https://doi.org/10.1016/j.actbio.2005.06.006>
- Wada, M., Heux, L., and Sugiyama, J. (2004)** Polymorphism of cellulose I family: Reinvestigation of cellulose IV₁. *Biomacromolecules*, 5: 1385–1391.
<https://doi.org/10.1021/bm0345357>
- Wang, C., and Wallace, G. G. (2015)** Flexible Electrodes and Electrolytes for Energy

Storage. *Electrochim. Acta*, 175: 87–95.
<https://doi.org/10.1016/j.electacta.2015.04.067>

Wang, H., Li, D., Yano, H., and Abe, K. (2014) Preparation of tough cellulose II nanofibers with high thermal stability from wood. *Cellulose*, 21: 1505–1515.
<https://doi.org/10.1007/s10570-014-0222-6>

Wang, Q., Yu, D. G., Zhang, L. L., Liu, X. K., Deng, Y. C., and Zhao, M. (2017) Electrospun hypromellose-based hydrophilic composites for rapid dissolution of poorly water-soluble drug. *Carbohydr. Polym.*, 174: 617–625.
<https://doi.org/10.1016/j.carbpol.2017.06.075>

Wang, Y., Lian, J., Wan, J., Ma, Y., and Zhang, Y. (2015) A supramolecular structure insight for conversion property of cellulose in hot compressed water: Polymorphs and hydrogen bonds changes. *Carbohydr. Polym.*, 133: 94–103.
<https://doi.org/10.1016/j.carbpol.2015.06.110>

Zheng, J., He, A., Li, J., and Han, C. C. (2007) Polymorphism control of poly(vinylidene fluoride) through electrospinning. *Macromol. Rapid Commun.*, 28: 2159–2162.
<https://doi.org/10.1002/marc.200700544>

Zhou, W., He, J., Cui, S., and Gao, W. (2011) Studies of Electrospun Cellulose Acetate Nanofibrous Membranes. *The Open Mater. Sci. J.*, 5: 51–55.
<https://doi.org/10.2174/1874088X01105010051>

Acknowledgement

First of all, I am very much thankful to “All mighty Allah” for his all kindest bless.

I am honored to pay sincere gratitude and special thanks to my supervisor, Professor Dr. Yasumitsu Uraki, for giving me the opportunity and tremendous support to work under his supervision, with his outstanding group. I would like to thank Dr. Keiichi Koda, who has provided me always positive attitude and quick responses, helpful criticism and dedication. This project could not be completed successfully without their guidance and assistance. This dissertation would not be fulfilled without their help. I would like to express special gratitude and appreciation to my all laboratory mates due to their kind help and support during experimentation.

I would like to thanks to Dr. Tajima Kenji for his expertise, knowledge and frequent help to use his space (room), Engineering Faculty for XRD measurement, Hokkaido University. Also, I would like to thanks to Saitou Takayuki for his expertise and knowledge for tribology measurement, Hokkaido Research Organization (HRO).

Last, but not the least, I would like to express my earnest appreciation to my beloved wife, Kbd. Shahinoor Islam, my child Shahriar Abdul Hadi and Khadiza-tul Kobra (Tohira) whom, they are miss me every moment during this journey especially my daughter (Tohira) who was not able to speak when I was started this journey and their moral support, endless love, patience, trust and understanding during my study.