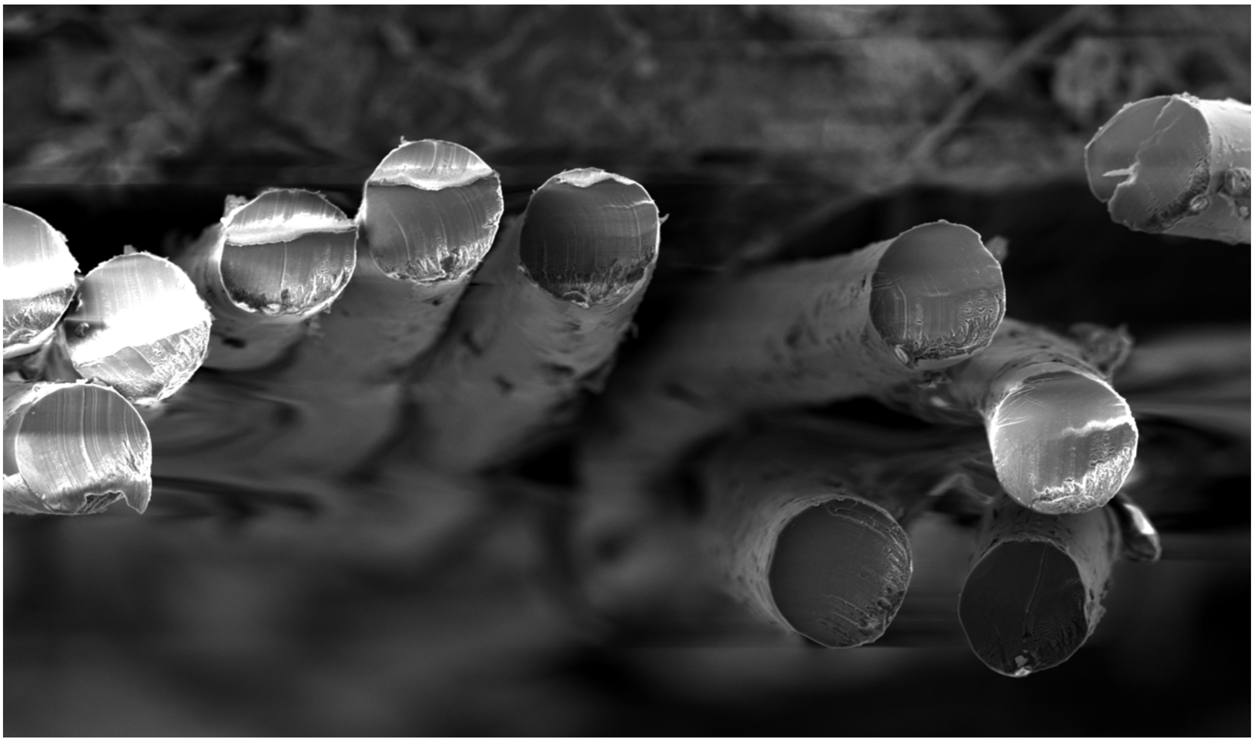


Effect of Drying Conditions on Lignin-Cellulose Carbon Fiber Precursors

Investigations of Porosity and Mechanical Properties

Master’s thesis in Material Chemistry

ERICA JOHNSSON

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2023
www.chalmers.se

Master's thesis 2023

Effect of drying conditions on lignin-cellulose carbon fiber precursors

Investigation of porosity and mechanical properties

ERICA JOHNSSON

Department of Chemistry and Chemical engineering
Performed at and in cooperation with RISE
Chalmers University of Technology
Gothenburg, Sweden 2023

Effect of drying conditions on lignin-cellulose carbon fiber precursors
Investigation of porosity and mechanical properties
ERICA JOHNSSON

Supervisor: Jenny Bengtsson, RISE
Examiner: Diana Bernin, Chalmers University of Technology

Master's Thesis 2023
Department of Chemistry and Chemical engineering
Performed at and in cooperation with RISE
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Cover:
Cross section of lignin-cellulose precursor fibers,
captures with a scanning electron microscopy.

Typeset in LaTeX
Printed by Chalmers Reproservice
Gothenburg, Sweden 2023

Effect of drying conditions on lignin-cellulose carbon fiber precursors
Investigation of porosity and mechanical properties
ERICA JOHNSSON
Department of Chemistry and Chemical engineering
Chalmers University of Technology

Abstract

Carbon fiber is a very attractive material because of its high strength-to-weight ratio, but the use is limited because of the expensive and fossil-based fiber precursors used today. A more cheaper and sustainable way is to use lignin-cellulose precursor fibers. Cellulose and lignin is that firs and second most abundant bio-polymer on earth and can be extracted in the Kraft process. By co-process these materials, cellulose can contribute with the strength in the fiber and lignin with the final yield after conversion. The final properties of carbon fibers are influences by the raw material, production of precursor fibers, and conversion to carbon fibers. This thesis focus on the effect of drying conditions on lignin-cellulose carbon fiber precursors by analysing the porosity and mechanical properties of the precursor fibers. In this thesis lignin and cellulose was dissolved using EMIMAc and shape using air-gap spinning. Different lignin ratios and drying conditions (free or with tension) were used. The examined porosity, using thermoporometry and water retention value, indicated decreased pore volume and swelling for fibers containing lignin. It also showed in major difference in pore volume for never dried fiber compare to dried which is related to the hornification of the fibers. When analysing the mechanical strength, the result showed an increase in strength for fibers dried with tension, especially for fibers containing lignin. Related to no significant difference in the porosity when comparing fibers dried free or with tension, the increase in strength is not related to the porosity. Instead it may be related to an increase of molecular orientation when drying with tension.

Keywords: Lignin-cellulose, Air-gap spinning, Drying, Porosity, Thermoporometry, Mechanical properties, Carbon fibers.

Acknowledgements

This thesis has been a part of the project Tandem Forest Values, a collaboration between RISE, Chalmers University of Technology, and Aalto University, financed by Formas. I would like to thank all of those who have contributed to the completion of this thesis. First and foremost, I would like to thank my supervisor Jenny Bengtsson for your guidance, feedback and always having time for my questions. I am truly grateful for the opportunity to work with you. I would also express my appreciation to Hanna Ulmefors for your support and discussions. Thirdly, I would like to thank Andreas Bengtsson for helping me with the conversion of pre-fiber to carbon fiber and for your help and feedback when evaluating the mechanical properties of carbon fibers. I am also very grateful for all help and support I have got from the Fiber unit at RISE Mölndal and for always showing interest in my work. I would also like to acknowledge Professor Thaddeus Maloney at Aalto University for very helpful feedback and discussion regarding thermoporometry. Finally, I would like to thank my examiner Diana Bernin for all support.

Erica Johnsson, Gothenburg, June 2023

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis listed in alphabetical order:

AGU	Anhydroglucose units
CF	Carbon fiber
DSC	Differential scanning calorimeter
EMIMAc	1-Ethyl-3-methylimidazolium acetat
MMCF	Man made cellulose fibers
NFW	Never freezing water
NMMO	N-methyl morpholine oxide
PAN	Polyacrylonitrile
PSD	Pore size distribution
PW	Pore water
SEM	Scanning electron microscopy
TPW	Total pore water
WRV	Water retention value

Contents

List of Acronyms **ix**

List of Figures **xiii**

List of Tables **xv**

1 Introduction **1**
- 1.1 Objectives 2

2 Theory **3**
- 2.1 Bio-based carbon fiber precursors 3
  - 2.1.1 Cellulose 3
  - 2.1.2 Lignin 4
  - 2.1.3 Solvent 5
  - 2.1.4 Spinning 6
  - 2.1.5 Porosity 7
- 2.2 Carbon fiber 8

3 Material and Methods **9**
- 3.1 Raw material 9
- 3.2 Solution of lignin and cellulose 9
  - 3.2.1 Rheology 9
- 3.3 Spinning 10
- 3.4 Drying 10
- 3.5 Characterization 10
  - 3.5.1 Mechanical strength - fiber precursors 10
  - 3.5.2 Microscopy 11
- 3.6 Conversion 11
  - 3.6.1 Mechanical strength - Carbon fibers 12

4 Method development **13**
- 4.1 Water retention value (WRV) 13
  - 4.1.1 Method WRV 14
- 4.2 Thermoporometry 14
  - 4.2.1 Method DSC 16

5 Results and discussion **17**

5.1 Porosity 18
5.1.1 DSC curve - Peak around -40°C 21
5.2 Fiber precursors properties 22
5.3 Carbon fibers 24

6 Conclusion **27**

7 Future work **29**

A Appendix 1 **I**

List of Figures

2.1 Molecular structure cellulose, including inter- and intra molecular hydrogen bonds. 4
2.2 Molecular structure the predominant monomers in lignin. **A.** p-comarly alcohol **B.** conifery alcohol **C.** sinapyl alcohol. 5
2.3 Molecular structure of EMIMAc 6
2.4 Different spinning techniques. From left to right: melt spinning, dry spinning, wet spinnins, and air-gap spinning. 7

3.1 Fiber precursors in crucibles and carbon frames before stabilization. . 11

4.1 Total pore water (blue) and nonfreezing water (green) dependent on moisture content. 15

5.1 Rheology curve of spin solutions. 18
5.2 Water retention value of fiber with different lignin ratio and drying techniques. 18
5.3 Measured total pore water divided, into never freezing water and pore water, using thermoporometry. 19
5.4 Pore size distribution. On the left: comparison between lignin rations, on the right: comparison between drying technique. 20
5.5 Exotherm preak between -38 and -48 °C for fiber precursors with different lignin ratios, L0, L30, and L50. 22
5.6 Mechanical properties fiber precursors. On the left, variation between different lignin ratios and drying free or on roll. On the right, comparison between DR1 and DR2 for L50 fibers, and different drying conditions. 23
5.7 Cross section of lignin-cellulose precursor fibers captured with a SEM. On the left, L0 fibers dried free. On the right, L50 fibers dried free. . 23
5.8 Mechanical properties of stabilized and carbonized fiber precursors. . 24

List of Tables

4.1 Water retention value for lyocell fibers. 13

5.1 Lignin and cellulose concentration, together with used draw ratio during spinning and used drying conditions. ND=never dried 17
5.2 NFW in total, as a monolayer in mesopores between 2-200 nm, and in micropores below the threshold where freezing occurs. 21
5.3 Comparison between TPW and WRV (ml/g), giving indication of the amount of pores larger than 200 nm. 21
5.4 Total yield of converted L50 fibers to carbon fibers. 25

A.1 Conversion to SI units from tensile strength of fiber precursors. I
A.2 Diameter of fiber precursors measured by Vibroskop, light microscope and SEM. Including standard derivation of the measured diameters. . I
A.3 Measured diameter of L50 fibers, never dried, dried and re-wet using light microscopy. Diameter measured in µm and converted into a volume assuming cylindrical shape and a length of 1. Using volume to prove the impact of an increase in diameter. The unit of volume is μm^3 I

1

Introduction

Carbon fiber (CF) is a commonly used material in wind turbines, sports, construction, aerospace, etc. since it has a high strength-to-weight ratio. Because of its previously mentioned properties, CF is a possible alternative material in the transport sector to improve the fuel economy by replacing steel and hence, decreasing vehicle weight. Today's commercial carbon fiber is mainly fossil-based and very expensive. The mainly used raw material for carbon fiber precursors is polyacrylonitrile (PAN) which is a fossil-based polymer and has a very high production cost[1]. To produce carbon fiber the carbon content is increased to above 90 wt%, this is done by stabilization and carbonization of precursor fibers.

In order to synthesize a more sustainable carbon fiber a renewable raw material would be favorable to use. Studies have shown a possible alternative to fossil-based carbon fibers is a combination of lignin and cellulose from wood [2, 3]. These materials are among the most abundant organic compounds in nature, and they are of high interest because they are inexpensive and biobased [4]. Both materials can be isolated from wood in the Kraft process where the product is cellulose, and the lignin can be extracted by the LignoBoots process from the black mass produces in the process. Lignin is suitable for biobased carbon fibers because of its high carbon content and can thus contribute with high yield. However, pure lignin fibers have not yet exhibited sufficient strength that requires for composite material. Cellulose on the other hand is stronger but is used to a limited extent because of its low carbon yield. A combination of lignin and cellulose has the possibility to result in an acceptable carbon fiber, with lignin that contribute with yield and cellulose with strength.[5]

Cellulose and lignin fibers can be produced by dissolving cellulose and lignin in an ionic solution and the fibers are shaped by using air-gap spinning, which is a type of wet spinning. The fibers are then coagulated in a coagulation bath with deionized water. There are other ways to produce biobased carbon fibers, but they will not be investigated in this thesis. One of the problems with bio-based carbon fiber precursors is that the strength is currently not high enough to replace commercial carbon fibers. Previous studies have improved the mechanical strength by increasing the tension during spinning, which influence the molecular orientation in the fiber favorable. Indication of similar effect of tension during drying have been seen.

The strength of a carbon fiber is also closely correlated to its porosity. Pores in fibers are defects that influence the mechanical properties of fibers. The porosity of fibers are affected by the molecular structure in the fiber. Therefore this work will focus on how the properties and the porosity of fibers with different lignin content can be influenced during drying.

This thesis is organized as follows: theory section provides a theoretical background of biobased fiber precursors including the raw, material, solvents, spinning, and porosity. Conversion of fiber precursors to carbon fibers is also be described. The material and methods section describes the material used and experimental part, where the used instruments and analytical method is included. A major part of the work consisted of method development for analysing the fiber porosity, and this is explained in a separate section. The result section presents the result and discussion on the porosity and properties of fiber precursors and carbon fibers. Finally, the conclusion of this work.

1.1 Objectives

The main objectives with this thesis was to analyse how fibers with different lignin content were affected by tension during drying. The lignin ratio and drying conditions were varied. This was analysed by the mechanical properties, pore size and swelling of fibers.

The same spinning parameters was used throughout the project, including same draw ratio, similar viscosity, and the same non-solvent in the coagulation bath. The only changing parameter in the dope was the lignin content. Same amount of cellulose was used for all solution and the same solvent, 1-ethyl-3-methylimidazolium acetate (EMIMAc). The fibers were dried in 60°C for 30 min, the difference was if they were dried with tension or free.

The overall hypothesis was that tension during drying would affect the porosity of the fiber and hence increase the mechanical strength. Additionally, that the tension would have more impact on fibers containing lignin compared to pure cellulose fibers. Method development of thermoporometry and water retention value (WRV) enabled usage of these methods to identify porosity in swelled fiber precursors. Thermoporometry and WRV will be further described in section 4.

2

Theory

Carbon fibers was mentioned for the first time in a patent by Thomas Edison 1879. He was using cellulose precursor fibers from cotton as the basis for his electric lamp. This was soon replaced, and it was much later in the 1950s the first commercial carbon fibers setup for cellulose fiber precursors was introduced [6]. From the 1950s to the 1970s, cellulose precursor fibers drew a lot of attention, but related to the discovery of PAN-derived carbon fibers, the research of cellulose based precursors decreased [7]. Together with the awareness of the climate changes and the promotion of finding material to replace fossil-based material, there is a huge increase of publication on lignin and cellulose used to produce carbon fibers since the 2000s. In this section, theory about the raw material, solvent, spinning, porosity and conversion to carbon fibers are specified.

2.1 Bio-based carbon fiber precursors

Bio-based carbon fibers precursors are made of dissolved cellulose with additional lignin. The benefits of using a combination of lignin and cellulose is that cellulose contribute with high strength and lignin with high yield of carbon fibers. Additionally, lignin and cellulose are inexpensive compared to the commercialized fibers precursors using today.

2.1.1 Cellulose

Cellulose is the most common bio-compound on earth. It can be found various plants and is incorporated in the cell wall and acts as the reinforcements. It is a linear polysaccharide composed of ahydroglucose units (AGU) linked with 1-4 glycosidic bonds, hydrogen bonds [4]. The hydrogen bonds make it possible for cellulose to bond with water even tho it has a hydrophobic nature between cellulose sheets, this make it an amphiphilic molecule. The degree of polymerization is around 3500-12000 in native cellulose and around 600-1500 in industrial pulps. The monomer units are connected with hydrogen bonds that gives a stiff molecule, illustrated in Figure 2.1. It has a semi-crystalline structure. Cellulose have four polymorphs, the main is cellulose I and cellulose II, the other two (III and IV) ar less common. Cellulose I is the form of native cellulose e.g wood, with cellulose sheets with parallel chains. Cellulose II is crystallized dissolved cellulose that are coagulated or regenerated. For cellulose II the chains are arranged anti-parallel to each other, resulting in a more thermodynamically stable crystalline form. Cellulose can not melt, at higher temperature the polymer will degrade. The cellulose have to be dissolved or chemical modified in order to form a liquid. [8]

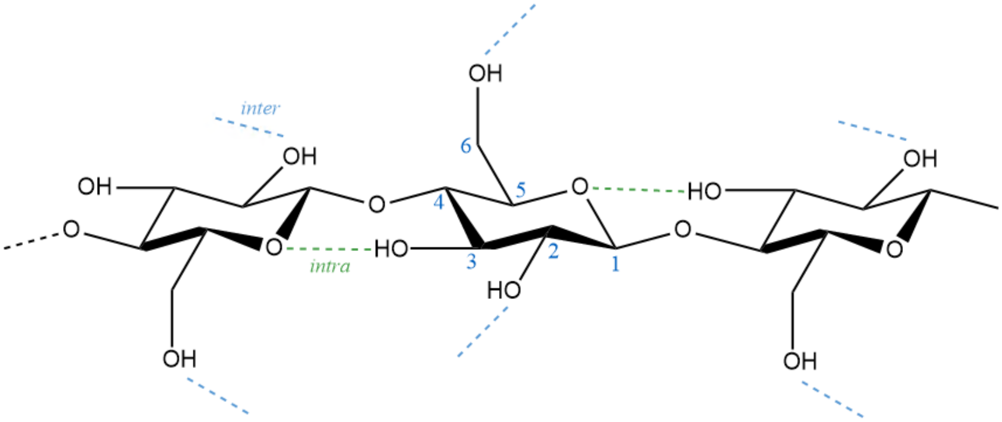


Figure 2.1: Molecular structure cellulose, including inter- and intra molecular hydrogen bonds.

The main source for processing cellulose is wood or wood pulp that consist of 40-50% cellulose. To extract cellulose form wood it have to be separated from the lignin and hemicellulose. This can be done by either the Kraft or Sulphite pulping process. The Kraft process is the dominant one and can be divided into cooking and bleaching. During the cooking the wood chips are preheated using steam and air is removed, further blended in a aqueous solution, the white liquor. This solution contains sodium hydroxide and sodium sulphite that break the chemical bonds in lignin. Lignin, hydroxy acids (carbohydrate related products), and additional extractives and formic acids are extracted with the solution. The out come is usually called black liquor. The pulp is then bleached to remove the residual lignin and increase the brightness. Dissolving pulp, which are used to spin regenerated cellulose fibers, contains relative low amount of lignin and hemicellulose. [9]

2.1.2 Lignin

Lignin is a complex macro molecule and one of the most abundant natural biopolymer. It is a hydrophobic polymer with a three dimensional and amorphous structure. Lignin can be found in different plants, mostly wood and grass that contain around 15-35% lignin. The polymer contribute with stiffness in the plant by filling in between cellulose and hemicellulose with the purpose of fixing them to each other. It is also important for transportation of water and nutrients, and work as a barrier against microbial degradation. The structure consist of monolignols that are biosynthesised to a heterogeneous and branching structure. There are three conventional monolignons, p-coumarly, conifery and sinapyl alcohols, Figure 2.2. Dependent on he structures formed in the polymer they are also referred to as hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units respective. Dependent on the type of wood, the ratio between the different monomers are different, softwood lignin consist mainly of guaiacyl while hardwood lignin have a mixture of guaiacyl and syringyl [4]. Lignin show thermoplastic properties which means that it have glass transition temperature (T_g), this make it possible to melt and further spin the lignin to fibers [10].

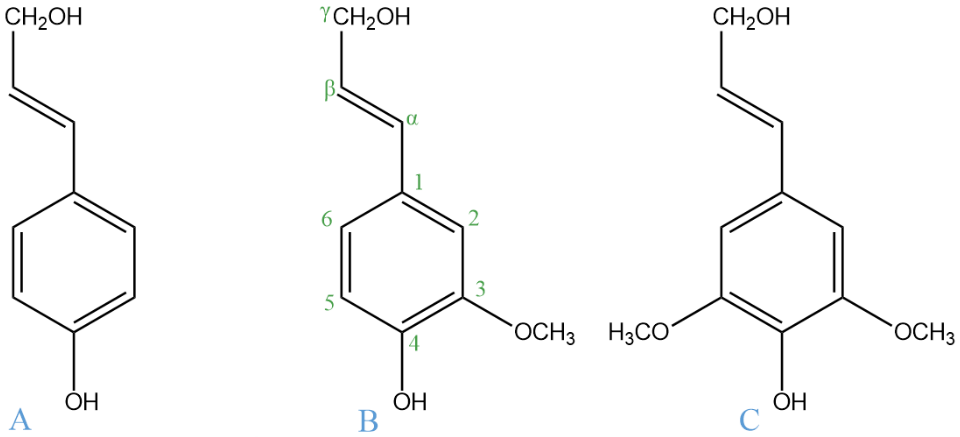


Figure 2.2: Molecular structure the predominant monomers in lignin. **A.** p-comarly alcohol **B.** conifery alcohol **C.** sinapyl alcohol.

In pulp production, lignin is derived from pulp together with the black liquor. The lignin can further be separated from the black liquor by the LignoBoost process. This process include two steps, the fist is separation of lignin from the black liquor by acidification of the liquor using CO_2 to pH 10. By lowering the pH the lignin participate out from the black liquor and the lignin can further be separated with a press filter. The lignin is then purified by first lowering the pH to 2 using H_2SO_4 to remove impurities and then pressed again before the final wash with water. The wet lignin are the dried. [11]

2.1.3 Solvent

To regenerate cellulose it have to be dissolved or chemical modified. There are only a few solvent that have the properties to dissolve cellulose because of the nature of cellulose, like high degree of polymerization and both hydrogen bonds and hydrophobic interaction within the polymer [8]. The most dominant process for the process of man made cellulose fibers (MMCF) is the vicsoce fiber process. In the process, carbon disulfide (CS_2) is used for derivatization of cellulose and sodium hydroxide ($NaOH$) is then used to dissolve it. The issue with this process is carbon disulfide that causes environmental issues and is a hazardous chemical that have to be controlled during production [12]. Lyocell is one other commercial MMCF, the solvent used in this process is N-methyl morpholine oxide (NMMO) that can direct dissolve cellulose. NMMO have the properties to dissolve cellulose high degree of polymerization and at high solid concentration, giving improved mechanical strength properties compared to viscose fibers. In addition, it can co-dissolve lignin and cellulose and can be recovered by evaporation if the non-solvent (water) in the spin bath. The disadvantages with the solvent is its thermally unsuitability that can lead to cellulose degradation if not stabilizers are added. One other class of solvent that can be used for dissolving cellulose is ionic liquids, these are salts with a melting point below 100 °C. Ionic liquids are composed of ions, an organic cation and on organic or inorganic anion. For dissolving of cellulose the cation serves as a hydrogen bond donor, and the anion serves as a hydrogen bond acceptor. In the present work, the ionic liquid used to dissolve lignin and cellulose is 1-ethyl-3-methylimidazolium acetate (EMIMAc), Figure 2.3, which is a solvent that has been extensively used in studies of cellulose fiber spinning [13]. EMIMAc is a liquid in room temperature, is more stable and NMMO, and can dissolve high amounts of lignin and cellulose at low temperature. The disadvantages with the solvent is its difficulties of recycling and risk for degradation of solvent and cellulose when store at high temperature.

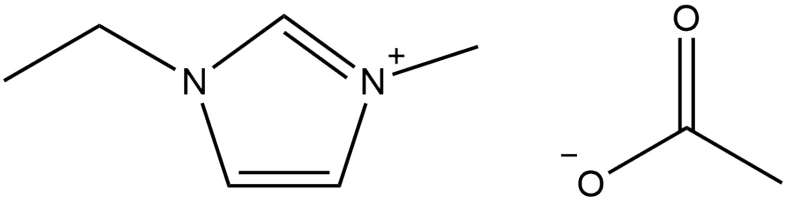


Figure 2.3: Molecular structure of EMIMAc

2.1.4 Spinning

There are three main types of spinning process, melt spinning, dry spinning and wet spinning, illustrated in Figure 2.4 [1, 6]. Dependent on the properties of the polymer, different spinning techniques are favorable. Melt spinning is used for polymers that can be melted while both dry and wet spinning are used for dissolved polymers. All techniques is based on the same principle, extrusion of a fluid through a die, solidification of the fluid, and some type of collection of fibers. It is in the solidification the differences between the types can be seen. For melt spinning a melted polymer solution is used. After forming the fiber through the die, cooling solidify the polymer. In dry spinning that uses a dissolved polymer, the fibers will be stabilized by evaporation of the solvent, resulting in solid fibers. For wet spinning, the fibers will be extruded in a non-solvent solution, resulting in coagulation of the fibers. There is also a modification of wet spinning, the air-gap spinning, also known as dry-jet wet spinning. This spinning technique have the die above the non-solvent, with an air-gap if 1 cm, and then coagulation of the fibers in the non-solvent.

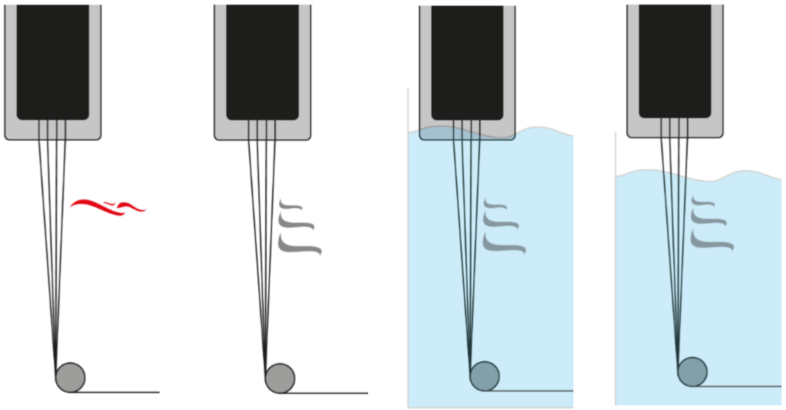


Figure 2.4: Different spinning techniques. From left to right: melt spinning, dry spinning, wet spinnins, and air-gap spinning.

For production of cellulose fiber both wet spinning and air-gap spinning are used. Viscose are produced by wet spinning and lyocell by air-gap spinning. A higher viscosity and elasticity of the solution are required for air-gap spinning compare to wet spinning. The gap allows stretching of the solution resulting in a more orientation of the polymer before coagulation. It also enable the use of different temperature for the die and the coagulation bath. The reason for using air-gap spinning for lignin and cellulose carbon precursor fibers is because the spinning process enable production of fiber with higher mechanical strength compared to wet spinning [6].

2.1.5 Porosity

Fiber defects like porosity or cracks is something that decreases the mechanical properties of both precursors and carbon fibers [14]. Pores are induced in the fibers during processing and can be affected during drawing by elongation and orientation of the pore, which can result in closure of the pores in the fibers [15]. Pores are affected during drying by collapse of pores when water evaporate. When drying the fibers, water will evaporate from pores, which in some case will lead to lower pressure in the pores, forcing the pore walls together. Previous studies have shown that larger pores (larger than 100 nm in diameter) first collapse and then smaller pores (smaller than 10 nm in diameter). Porosity affect swelling properties and is related to water absorption of the material. Pore characteristics including pore volume, shape and pore size distribution are parameters that affect the swelling capability and mechanical properties [16]. Drying will additional affect the polymer structure because of hornification. This phenomenon describes chemical and physical changes of cellulose fibers during drying and wetting. The stiffening of the polymer is related to formation of irreversible bonding in the fiber upon drying [17]. This hinder swelling of fibers during re-wetting and may contribute to closure of small pores.

2.2 Carbon fiber

To define a carbon fiber, the carbon content of a fiber must exceed 90 wt%[6]. This can be done by first stabilization and then carbonization and/or grapthitazation of the fiber precursor. During the stabilization, oxidation of the fiber precursors occurs to prepare it for the carbonization. This prevent merge of fibers, lost of shape and formation of hollow fiber cores. Different types of reactions occurs during stabilization for instance, oxidation, dehydration, dehydrogenation, crosslinking and cyclization, dependent on both precursor and condition used (heating rate, final temperature, dwell time and tension)[18]. Stabilization effect the yield and tensile properties. The conversion yield of cellulose fibers can be increased because the oxidative stabilization can prevent formation of unstable compounds that effect the yield negative. Dependent on the desired final quality of the fiber, a temperature between 200-300 °C is used during stabilization. To get the desired characteristics of the final fiber there is a trade off between cost and quality, the closer the stabilization temperature is to the degradation of the fiber precursors, the faster is the stabilization, but the high temperature can affect the quality of the final fiber. In a continuous conversion process the stabilization step is the most consuming and can take hours while the canonization only takes minutes. This leads to the most cost consuming step. Carbonization, on the other hand, takes place at a higher temperature usually between 1000-1700 °C. In this step the carbon content is concentrated and purified by using heat in the absence of oxygen to remove organic matter. During this step elements like oxygen, nitrogen and hydrogen removes which results in a carbon content of at least 90 wt%. Settings like temperature profile, residence time, tension and gas flow etc. depends on the precursors and the desired characteristics of the final fiber. To increase the carbon content further graphitazation can be added but it is not required. [6]

3

Material and Methods

The prepared biobased precursor fiber analyzed in this thesis were made of lignin and cellulose dissolved in an ionic solvent EMIMAc. This mixture was then shaped to fibers using air-gap spinning. The final fibers were then analyzed and evaluated by different methods, which are specified in the following sections.

3.1 Raw material

The used material to produce fibers was softwood kraft lignin produced at the LignoBoost Demo (Bäckhammar, Sweden) with the LignoBoost process. The Klason lignin content of the lignin was 94% [5]. Cellulose obtained from a softwood Kraft dissolving-grade pulp produced by Georgia Pacfic (Atlanta, GS, USA) with an intrinsic viscosity of 465 ml/g determined according to ISO 5351:2010. The ionic liquid 1-ethyl-3-methyl imidazolium acetate (EMIMAc, 95%) was purchased from Sigma-Aldich (Steinhemin, Germany).

3.2 Solution of lignin and cellulose

The pulp was ground to improve the solvent impregnation of the pulp. First, the pulp and EMIMAc were mixed. Lignin powder was then added stepwise to the mixture with blending in between to avoid clumps of lignin in the mixture. The mixture was blended in a closed reactor, heated to 70°C and stirred at 30 rpm for one hour using an anchor impeller. After blending, the mixture was transferred to the container used during spinning and deareation was performed at 60°C below 10 kPa pressure for at least 12 h to remove excess air from the mixture. The final mixture was then characterized by rheology measurements.

3.2.1 Rheology

Oscillating rheometry was used to analyze the viscoelastic properties of the solution, the analysis was performed using a NOVA Melts Rheometer (Reologica Instuments AB). To obtain the temperature-viscosity relationship of each spin solution a cone/plate-geometry (40 mm/4°) and strain of 0.01 were used. The analysis was carried out for all spin solutions at constant temperatures of 45°C and 60°C. For the result, viscosity and frequency was plotted against each other.

3.3 Spinning

The air-gap spinning of the fibers was performed with a bench setup system. For the pump, a velocity of 2 mm/min was used, which corresponds to an extrusion speed of 4 m/min from the die. The draw ratio (DR) 2 was used for all fibers with lignin, which means that the velocity of the collective rolls was 8 m/min. For cellulose fibers DR 1 was used to get a similar thickness as for the fibers containing lignin. The dope was extruded through a 33-hole spinneret with a capillary diameter of 100 μm and a length to diameter ratio (L/D) of 2. The container for the solution had a heat mantel to ensure that the solution had a temperature of 45°C or 60°C dependent on solution used. There was a one centimeter gap between the die and the coagulation bath. The coagulation solvent used was deionized water with a temperature below 5°C. The fibers were collected on rolls, and the rolls with fibers were stored in deionized water below 10°C.

3.4 Drying

Two types of dried fibers were attained, dried on spinning rolls (tension) and free drying. Both samples were dried in an oven at 60°C for 30 min, to a dry content of 95%. Never dried fibers were used for comparison to analyze the effect of drying. The diameter was measured for both types of drying to analyze the changes in diameter after drying.

To analyze how more tension during drying affects the porosity and changes in diameter , measurements of single tows with different weights were conducted. They were dried at the same temperature and time as previously mentioned.

3.5 Characterization

Pore size, density, surface area, mechanical strength and swelling of the precursor fibers were analyzed with different types of instruments. In the following sections, mechanical strength and microscopy will be described. The methods used for swelling of fibers and pore size distribution are further explained in section 4.

3.5.1 Mechanical strength - fiber precursors

The mechanical strength of a fiber was analyzed by first measuring the titer ($dtex$), which is the linear density of the fiber. This was done using a Vibroskop (LEnzing Instruments, Lenzing, Austria) that induces vibration and then adjusts the length of the fiber to obtain resonance. The titer was then used to measure the tenacity and elastic modulus (cN/tex) with a Vibrodyn (Lenzing Instruments). This instrument performs a tensile stretch of the fiber until breakage. All measurements were performed in a controlled climate with a temperature of 20 ±2°C and relative humidity of 65 ±4%. Conversion to SI units (Pa) was done based on fiber density that was measured using He-pycnometer Accupycll 1340 (Micrometrics instrument) at room temperature.

3.5.2 Microscopy

Both light microscopy and scanning electron microscopy (SEM) were used to analyze the fibers. Light microscopy was used to analyze the swelling of the fibers. The thickness of dried, swelled, and never dried fibers was measured. For the swelled fibers some water was added.

The dried fibers were examined using a JSM-6610LV F (JEOL, Tokyo, Japan) SEM in a high-vacuum mode to analyse the surface and cross section. The microscope was operated at an acceleration voltage of 5 kV and a working distance (WD) of 10 mm. The fibes were mounted on carbon conductive tape, cut with a razor blade, and sputtered with a Pt layer of 1.5 nm using a Cressington 208HR sputter coater (Cressington Scientific Instrument Ltd., U.K.).

3.6 Conversion

The conversion of precursor fibers to carbon fibers was carried out at RISE in Stockholm. The single fiber precursors were fixed to carbon frames to prevent shrinkage and attached with carbon adhesive that were left overnight to dry. The precursor fibers were placed in a muffle furnace for oxidative stabilization. The air flow in the furnace was 7 L/min and it was heated from 25°C to 250°C with a heating temperature of 5°C/min, the isothermal time at 250°C was 1 h. Carbonization was carried out in a ceramic tube furnace with a nitrogen flow of 300 ml/min and heating from 25°C to 1000°C with a heating temperature of 3°C/min. The isothermal time at 1000°C was 30 min. The same procedure was used on dried L50 fibers but in crucibles instead of carbon frames to get a lager amount of fibers to analyse and gravimetric yield determination, Figure 3.1.

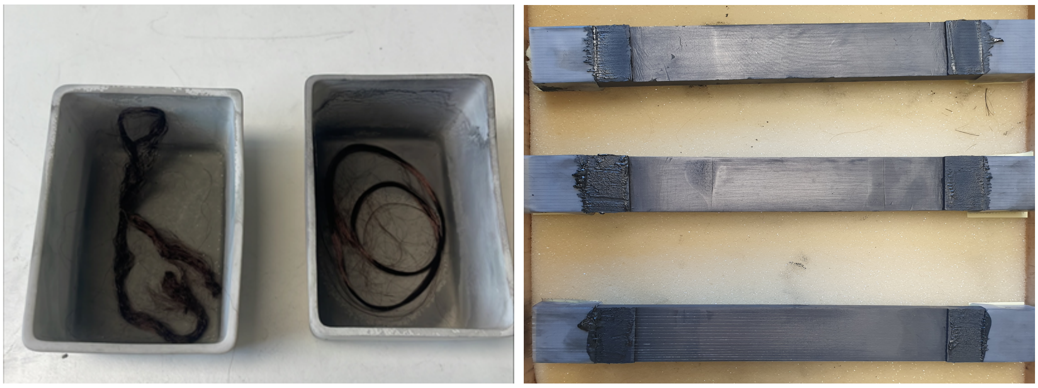


Figure 3.1: Fiber precursors in crucibles and carbon frames before stabilization.

3.6.1 Mechanical strength - Carbon fibers

Single fiber tensile test of the carbon fibers was performed in a single-filament tensile tester from Diastron Ltd. This instrument is developed for tensile test of glass and carbon fibers. A laser diffraction system is used for diameter determination of carbon fibers. All fibers were analysed with a fixed gauge length of 20 mm and a elongation speed of 0.6 mm/min was used. The test was carried out at 21°C and 31% relative humidity. 18 individual filaments was measured to obtain an average. Young's modulus and tensile strength were measured in GPa repsective MPa, and the diameter in µm.

4

Method development

In this section water retention value (WRV) and thermoporometry will be further explained. The method development of each method will also be described.

4.1 Water retention value (WRV)

WRV is a measure of how much water a fiber can absorb [19, 20]. It is mainly used for pulp fibers and it gives a indication of the volume of pores in the material. In this work, WRV was used to obtain a relative value compared to total pore water (TPW) measured using DSC, further described in the section below. According to the ISO standard the pulp should be analysed as a test-pad. In order to make this analyse suitable for continuous fibers that are not able to form as a pad, the method had to be further adjusted.

To find a suitable amount of fibers needed for the method, lyocell fibers were used. Lyocell fibers are produced in a similar way as cellulose precursor fibers but with a higher draw ratio contributing to a higher crystallinity. Different amounts of dry lyocell fibers, 50, 100, 200, 400, 800, and 1000 mg, were used. The results are shown in table 4.1, and indicates that when using a small amount of fibers the WRV are higher. A higher WRV for lower mass indicates that the contribution from water between the fibers cannot be neglected. The result was compared with the previous literature that indicates that dried lyocells have a WRV between 0.6 and 0.8 ml/g.

Table 4.1: Water retention value for lyocell fibers.

$Fiber(mg)$	50	100	200	400	800	1000
$WRV(ml/g)$	0.98	0.76	0.76	0.73	0.69	0.81

From the result it was concluded to use at least 100 mg of fibers was needed to get a reliable result. Difficulties with this method is the weighting after the centrifugation. If the container is open, the water evaporates, resulting in a decrease in the amount of water in the fiber. If a closed container is used instead, the problem is that when the fibers are transferred to the container, some of the water can get lost. Therefore the amount of fibers have to be high enough so this water loss can be neglected.

When the whole fiber was placed in the filtration tube, the structure varied depending on whether the fibers were dried on a roll or free. If the fibers were dried free, the structure was more like a web but when the fibers were dried on roll, the fibers kept the straight structure. The problem with this is that more water "get stuck" in a web compared to the straight structure and therefore give a higher WRV. Therefore, were all fibers cut into 1 cm pieces to get a more similar structure for both dried and never dried fibers, and also simplify the preparation of DSC measurements.

4.1.1 Method WRV

For the measurement 100-200 mg dried fibers were used. All fibers were cut into 1 cm pieces and soaked in deionized water for 1 h before placing them in the centrifuge filter tube 50 ml, 30 x 115 mm style. The filter used was Whatman GF/C glass microfiber filters 1.2 µm and the used instrument for centrifugation was MPW-352 centrifuge (MPW MED. Instruments). A centrifugal force of 3000 ±50 g (g is the acceleration due to gravity, i.e. 9.81 m/s^2) for 30 min ±30 s according to ISO 23714:2014 was used for centrifugation. Fibers were transferred to a pre-weighed eppendorf tube that had been dried in an oven at 105°C for at least 1 h. The wet fibers were weighed in milligrams with two decimals. The tube with fibers was placed in the oven with open lid at 105°C over night, no longer than 24 h. The fiber-containing tube was closed and cooled before weighing the dry fibers. WRV was calculated with the equation 4.1.

$$WRV = \frac{m_1}{m_2} - 1 \tag{4.1}$$

m_1 is the mass of the centrifuged wet sample in grams.
m_2 is the mass of the dry sample in grams.

4.2 Thermoporometry

Thermoporometry is a method can be used to analyze the pore size distribution of various mesoporous materials including cellulose fibers. This method is only applicable to analyses in water systems because it is based on phase transitions. It is one of few methods that can measure wet, never dried, samples, many other methods demand dry samples. Therefore it is a suitable method for analysis of cellulosic materials because of the hornification that affect structure and pores upon drying, as earlier mentioned in 2.1.5. Thermoporometry is based on the depressed melting temperature of water held in pores which can be measured using a differential scanning calorimeter (DSC). The depressed melting temperature is related to the lower pressure at curved surfaces in pores [16]. By using the Gibbs-Thomson equation, the changes melting temperature can be used to calculate the diameter of the pores. The analysis give a value of never-freezing water (NFW) and pore water (PW). NFW is the monolayer of water on the surface that does not freeze, due to interactions between water and the surface. This can be calculated knowing the total amount of water added to the sample and comparing to the calculated total amount of water in the sample by measuring the endothermic peak (melting) when increasing the temperature from -50°C to room temperature. The PW is calculated form the exothermic peak (freezing) when decreasing the temperature from -0.2°C to -20°C. The total pore water (TPW) is the sum of NFW and PW. NFW is included in the total pore water because most of the fiber surface area is located in the fiber pores [16]. For the analysis an isothermal step melting is used, this means that the temperature is increased to a point where the it is held constant in order to find equilibrium. This has been shown to be favorable for cellulostic materials because it allows us to neglect the effects of thermal lag [21].

To make the method suitable for cellulose and lignin fibers, different DSC programs with different heat and cooling rates and different isotherms were analyzed. The most suitable method was cooled down to -50°C, heated to -0.2°C and then cooled down to -50°C again and finally heating to room temperature. Two isotherms were used, one at -50 after the first cooling, and one at -0.2. When deciding which program to use, different moisture content-50°C or the sample was tried. Previous studies have proved that the NFW will increase with increased moisture content to a point where it then becomes constant, the same for TPW but at a higher moisture content [16]. From this it can be assumed that the surfaces are first covered, then the pores, and the excess of water is bulk water. Therefore, the different moisture content of the cellulose and lignin fibers was analyzed according to Figure 4.1. The fibers was first cut into 1 cm pieces and soaked in water for at least 1 h, then centrifuged according to settings for WRV to have filled pores without additional water. The samples were prepared in an aluminum pan by adding 6-8 mg of wet fibers and adding water, the pan was sealed and placed in the DSC instrument for analysis.

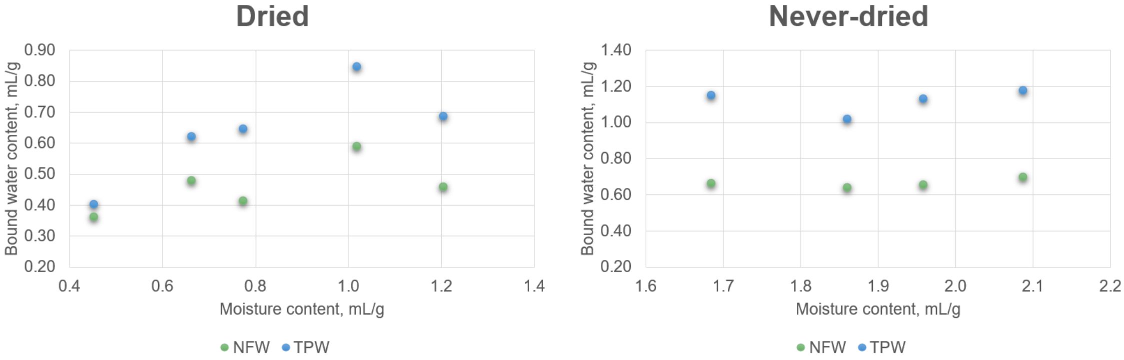


Figure 4.1: Total pore water (blue) and nonfreezing water (green) dependent on moisture content.

The result shows that for dried fibers the NFW and the differences between NFW and TPW are almost constant after adding 2.5 µl which correlates to a content of 0.8 ml/g for dried L50 fibers. Constant NFW and TPW indicates that both the surface and the pores are filled. For never dried fibers with no additional water the moisture content is almost 1.7 ml/g and has already a constant NFW and TPW when comparing to higher moisture contents. But to ensure that there is some bulk water in the sample 1 µl water is added to the sample.

4.2.1 Method DSC

The DSC measurements were made on a DSC 1 STARe System (Mettler Toledo). The samples were prepared in an aluminum pan by adding 6-8 mg wet fibers from WRV and additional water. A sample with only water was used in order to calculate the specific heat of fusion of water (H_f). The pan was sealed and placed in the DSC instrument. Analysis of water was done at the beginning and end of the whole analyse. The set-up of the program started to go down from 20°C to -50°C with a 10°C/min rate and hold at -50 °C for 10 min. Went up to -0.2°C with a 5°C/min rate and hold for 15 min. Decreased the temperature to -50°C with a rate of 2 °C/min, went up to 20 °C with a heating rate of 5°C/min. The results were used to calculate never freezing water (NFW), pore water (PW), and total pore water (TPW) using these equations 4.2, 4.3, and 4.4.

$$NFW = W - \frac{\Delta H_{endo}}{H_f} \tag{4.2}$$

H_f is the specific heat of fusion of water calculated from the result of the water analyzes. ΔH_{endo} is the sample melting enthalpy when going from -50 - 20°C.

$$PW = \frac{\Delta H_{exo}}{H_f} \tag{4.3}$$

ΔH_{exo} is the sample freezing enthalpy when freezing from -0.2 - -20°C. The approximate total pore water can then be calculated using NFW and PW.

$$TPW = NFW + PW \tag{4.4}$$

The pore size distribution (PSD) was analyzed using the exotherm peak from -0.2 down to -20°C and calculate relative intensity by dividing the intensity (I) with the sum of I between -0.2 and -20, and then multiplying with the TPW. The cumulative relative I was then plotted against the diameter D which was calculated by using the Gibbs-Thomson (GT) equation 4.5.

$$D = \frac{k}{\Delta T} + T_{mono} \tag{4.5}$$

k is the GT coefficient 43 nm/°C and T_{mono} is the monolayer thickness of water 0.28 nm. By using this equation a pore size distribution between 2-200 nm can be covered.

5

Results and discussion

In this investigation, cellulose-lignin precursor fibers with different ratios were made to analyze the effect of the drying method on mechanical strength and porosity. All fibers used are presented in Table 5.1 together with the concentration of cellulose and lignin, the draw ratio used during spinning and the drying method. The fibers are discussed further in the result using the name displayed in Table 5.1.

Table 5.1: Lignin and cellulose concentration, together with used draw ratio during spinning and used drying conditions. ND=never dried

Ratio	Cellulose, wt%	Lignin, wt%	Total polymer conc, wt%	DR	Drying	Name
L0	8	0	8	1	ND	L0 ND
				2	free	L0 free
				1	on roll	L0 on roll
L30	8	30	11.4	2	ND	L30 ND
				2	free	L30 free
				2	on roll	L30 on roll
L50	8	50	16	2	ND	L50 ND
				2	free	L50 free
				2	on roll	L50 on roll

Rehological measurements give the dynamic behavior of the solution. To make it possible to apply some tension during spinning without breaking of filaments, the solution should exhibit both viscous and elastic properties. This means that it should have a Newtonian plateau with a constant zero-shear viscosity. If the solution instead does not have any constant viscosity, no Newtonian plateau, and the zero-shear viscosity approaches infinity, it is more like a gel than a solution, meaning that it requires a certain applied stress to flow. A gel behaves much more elastic than viscous and thus isn't suitable to form fibers. As can be seen in Figure 5.1 all solutions have a tendency of a plateau meaning that all have properties for solutions and not gel. In addition, all solutions are highly viscous, meaning that they are suitable for air-gap spinning. An increase in temperature decreases the viscosity of the solvent. Therefore, all solutions was analysed at constant temperature (45°C and 60°C) to see how to adjust the temperature to get similar viscosities. The temperature used during spinning is the same as shown in Figure 5.1.

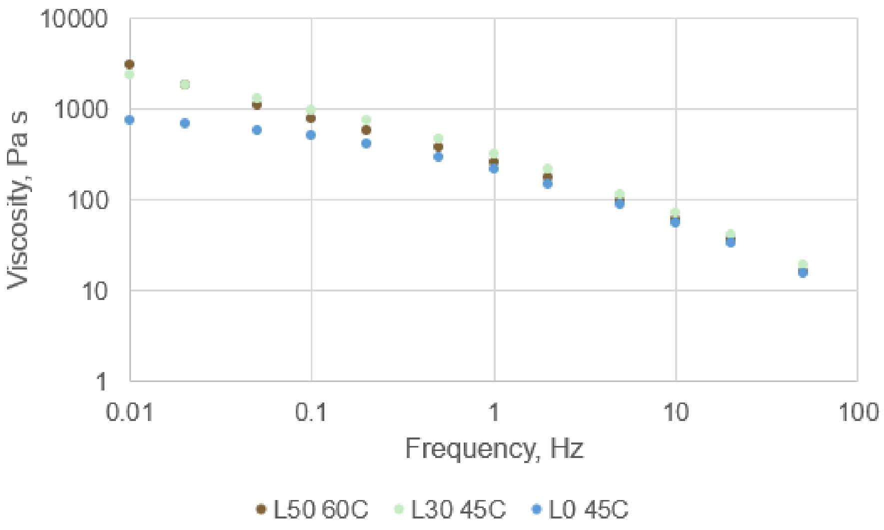


Figure 5.1: Rheology curve of spin solutions.

5.1 Porosity

The porosity in the water swelled fibers was analyzed using WRV and thermoporometry. The WRV results are illustrated in Figure 5.2. As can be seen, there is a large difference in WRV between never dried and dried fibers, which is a result of hornification and shows the impact of drying. There is also differences between fibers with different lignin ratios, when the lignin content increases, the WRV decreases. However, the conditions during drying, with or without tension, has no significant impact on the WRV

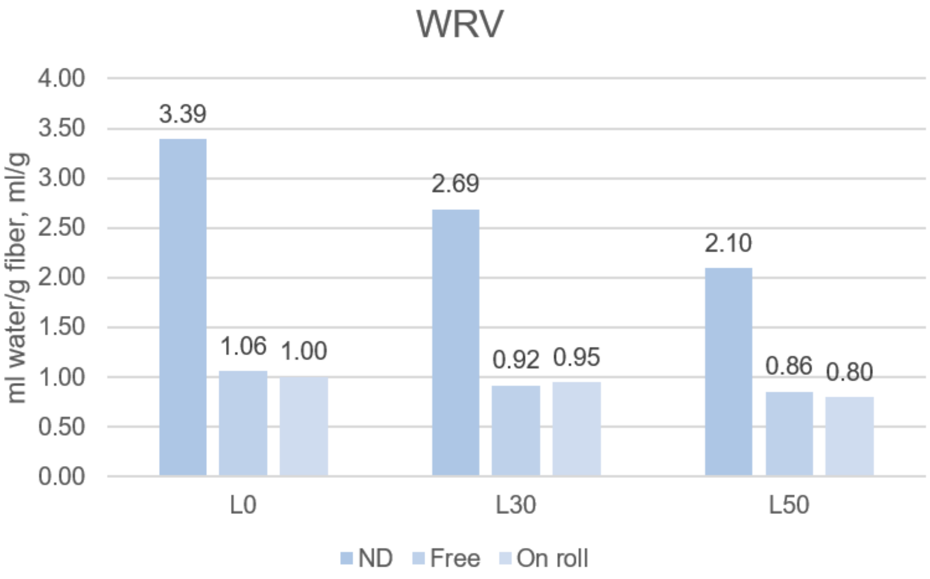
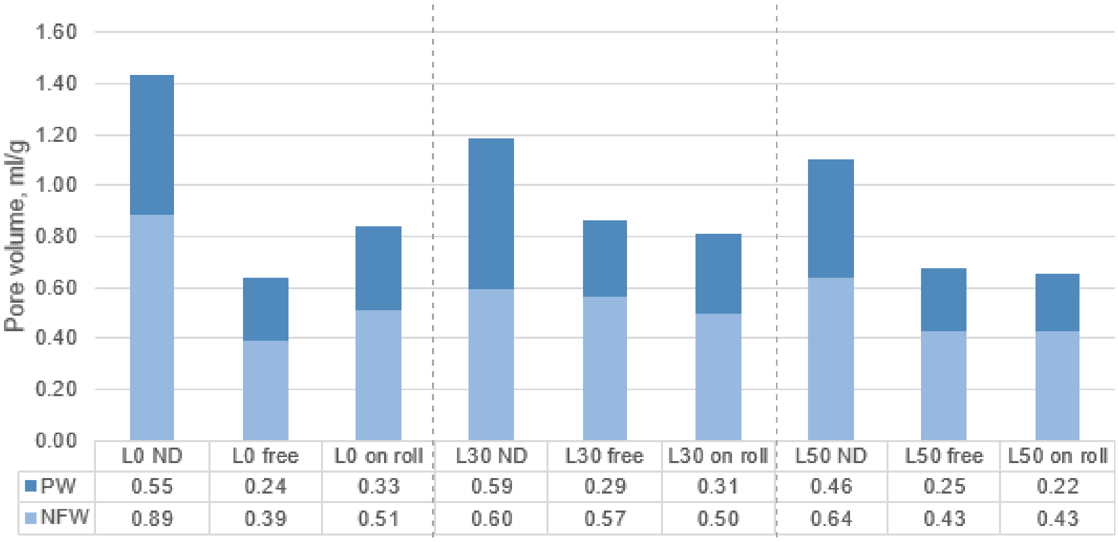


Figure 5.2: Water retention value of fiber with different lignin ratio and drying techniques.

The WRVs of never dried fibers are very high compared to never dried pulp fibers that have a WRV of around 1.4 ml/g [20, 22]. The probable reason for the lower WRV of pulp fibers is that the cell wall in pulp fibers prevent the fibrils in the fiber to swell. Studies have shown an increase in WRV when increasing the beating time or removal of lignin, both of which loosen the cell structure [20, 23]. Regenerated cellulose fibers do not have any cell structure, instead there is a three dimensional network of cellulose. Hence, there is nothing that prevents the fibrils to swell.

Fiber diameters have been measured to verify the WRV result. The diameter for never dried fibers are almost twice as the diameter for dried fibers. This means that the total volume will be about four times larger for never dried compared to dried. By doing a similar calculation as for WRV, i.e. calculating the volume of the swelling, gives a result of 2.3 ml/g and 0.9 ml/g for never dried and dried on roll L50 precursor fibers, respectively. Thus, the WRV were considered reliable. The measured diameters are available in the Appendix A.

To further look in to the pore size distribution, thermoporometry was used. The result gave an indication of never freezing water (NFW) and total pore water (TPW) in the fibers. The result is illustrated in Figure 5.3, showing the NFW and PW that together gives the TPW. It follows the same pattern as the result from WRV, with a decreased total pore volume with increased lignin ratio.



	L0 ND	L0 free	L0 on roll	L30 ND	L30 free	L30 on roll	L50 ND	L50 free	L50 on roll
■ PW	0.55	0.24	0.33	0.59	0.29	0.31	0.46	0.25	0.22
■ NFW	0.89	0.39	0.51	0.60	0.57	0.50	0.64	0.43	0.43

Figure 5.3: Measured total pore water divided, into never freezing water and pore water, using thermoporometry.

The pore size distribution (PSD) is interesting to analyse because it has a large impact on the surface area, many small pores can contribute to a higher surface area compare to a fiber with few larger pores. This was calculated using the Gibbs-Thomson equation 4.5 and the cumulative intensity from the DSC measurements was correlated with the TPW. The result has been plotted in graphs, illustrated in Figure 5.4. Comparisons between different lignin ratios and drying conditions are illustrated. The total pore volume decreases, significanlty when the lignin content increases and slightly when the tension increases during drying. The largest difference in pore volume is between dried and never dried fibers, which is related to hornification. The pore size distribution is interesting because it has a large impact on the surface area. Many small pores can contribute to a higher surface area compare to a fiber with few larger pores.

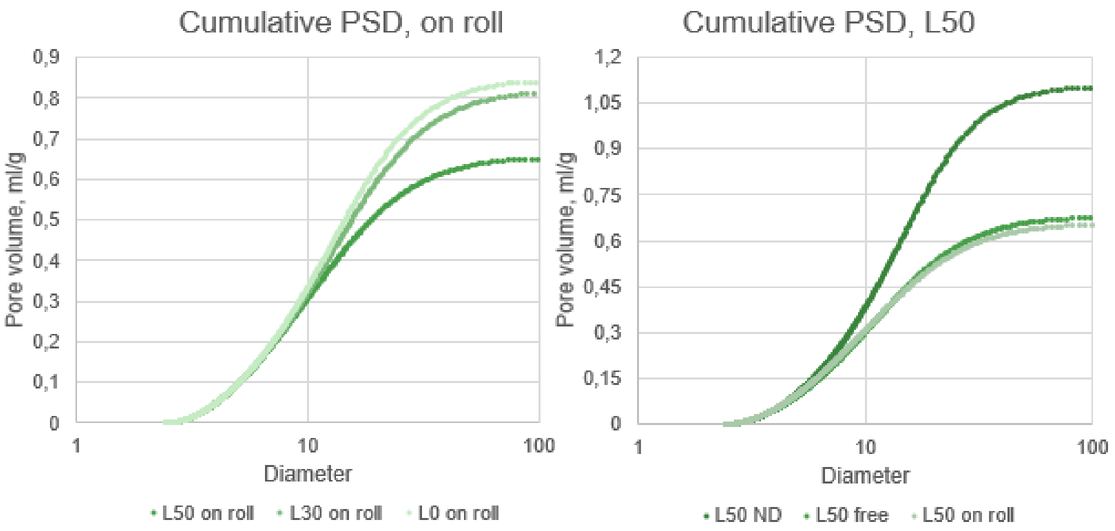


Figure 5.4: Pore size distribution. On the left: comparison between lignin rations, on the right: comparison between drying technique.

The measured NFW is the sum of a water monolayer in mesopores and water in small pores with a diameter smaller than required for water to form an ice crystall. The total monolayer of NFW in pores have been calculated from the PSD curve by assuming cylindrical pore geometry. By using the Gibbs-Thomson equation the temperature was converted into a volume. The intensity (mJ) for all temperatures from the DSC curve was used to get the amount of pores with a certain volume. From that the volume of the monolayer of NFW in mesopores can be calculates. In Table 5.2 the total NFW, the monolayer of NFW in the mesopores, and the NFW in the subfreezing micropores are presented. It shows that the majority of NFW is within micropores, that include pores smaller than 2 nm, water on the surface and nonfreezing monolayer in pores larger than 200 nm. The result also shows that that there is about equal amount of NFW monolayer in mesopores for all dried samples and more differences in the amount of NFW in subfreezing micropores. There is a decrease of NFW in mesopores after drying which indicate some type of closure of pores with a diameter of 2-200 nm.

Table 5.2: NFW in total, as a monolayer in mesopores between 2-200 nm, and in micropores below the threshold where freezing occurs.

Sample	Total NFW, ml/g	Monolayer NFW in mesopores, ml/g	NFW in subfreezing micropores, ml/g
L50 ND	0.64	0.18	0.46
L50 free	0.43	0.07	0.35
L50 on roll	0.43	0.08	0.35
L30 ND	0.60	0.19	0.41
L30 free	0.57	0.10	0.47
L30 on roll	0.50	0.09	0.41
L0 ND	0.89	0.25	0.64
L0 free	0.39	0.07	0.33
L0 on roll	0.51	0.10	0.41

By combining thermoporometry and WRV more information can be concluded from the result. WRV give a result of the entire pore volume in the sample and thermoporometry give more specific information of pore size distribution and NFW that can be used to give an indication of the total surface area of the pores. By comparing the thermoporometric TPW and the WRV, an indication of the volume of pores larger than 200 nm can be calculated. The results are shown in Table 5.3. This illustrates that never dried fibers, independent on lignin ratio, contain many more large pores than dried fibers. Furthermore, this demonstrates the impact of drying and shows that a major share of the larger pores collapse upon drying.

Table 5.3: Comparison between TPW and WRV (ml/g), giving indication of the amount of pores larger than 200 nm.

	TPW	WRV	Pores >200
L0 ND	1.43	3.39	58%
L0 free	0.64	1.06	40%
L0 on roll	0.84	1.00	16%
L30 ND	1.19	2.69	56%
L30 free	0.86	0.92	6%
L30 on roll	0.81	0.95	14%
L50 ND	1.10	2.10	48%
L50 free	0.67	0.86	21%
L50 on roll	0.65	0.80	19%

5.1.1 DSC curve - Peak around -40°C

When analysing the DSC curves there is a small peak around -40°C that is not a part of the pore water described by the Gibbs-Thomson equation. Notable is that this peak is only obvious for fibers containing lignin. Both L0 fibers that contain only cellulose and lyocell fibers only show a slight peak tendency in this temperature range, see Figure 5.5. The main difference between these fibers is that cellulose has a more crystalline structure, while lignin is more amorphous. Meaning that the peak could come from glassy phase of water in amorphous domains. The peak at -40°C was also more distinct for never dried L50 fibers compared to dried. This decrease could be due to an alignment of the amorphous domains during drying.

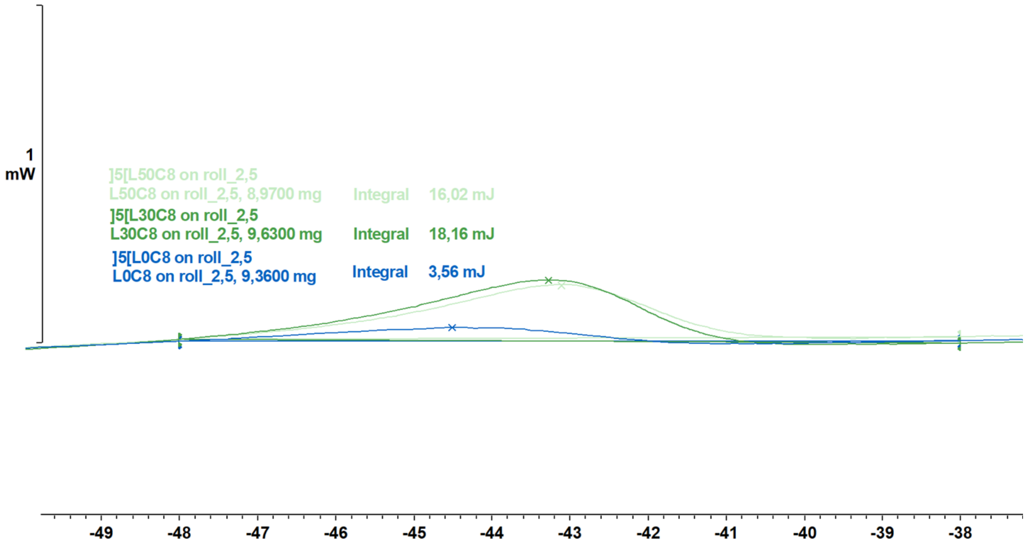


Figure 5.5: Exotherm preak between -38 and -48 °C for fiber precursors with different lignin ratios, L0, L30, and L50.

5.2 Fiber precursors properties

The variety of characteristics between lignin and cellulose like molecular weight and crystallinity etc., make it interesting to analyse how different properties are affected by different lignin ratios and different drying conditions. The mechanical strength, density, fiber morphology, and diameters were analyzed. Density was mainly used to convert the linear density to diameter.

The density of the fibers shows that the it decreases as the lignin content increases. This is likely related to the lower molecular weight of lignin compare to cellulose or the packing of molecules. A more structured molecule can have a closer packing which increase the density. Both molecular weight and structure also affect the tenacity and modulus of the fibers. Indications of this have been seen when analysing the mechanical properties of the fibers, a higher lignin content gave a lower tenacity, which was expected, probably because of the non-linear structure of lignin.

When analyzing the effect of using tension during drying, it is found that those fibers dried with tension have higher tenacity and modulus. This effect was particulary clear for fibers that contained lignin. Similarly, results for L50 fibers with applied tension during spinning, i.e., increased draw ratio improved the mechanical properties, see Figure 5.6 for comparison between DR1 and DR2. Similar results have been stated in other studies analyzing mechanical properties of fibers spun with different draw ratio [24]. The differences between using draw ratio or tension during drying is that during spinning, the draw ratio affects the fibers before and during coagulation, i.e. in the air-gap and in the water. When tension is applied during drying, the fibers have already coagulated but as can be seen from the results in this study especially cellulose-lignin fibers are still flexible. By combining a high draw ratio during spinning and tension during drying, the mechanical properties may be further improved. The mechanical strength of the final carbon fiber could also be improved by stretching during the stabilization in the conversion process of lignin and cellulose fiber precursors [25].

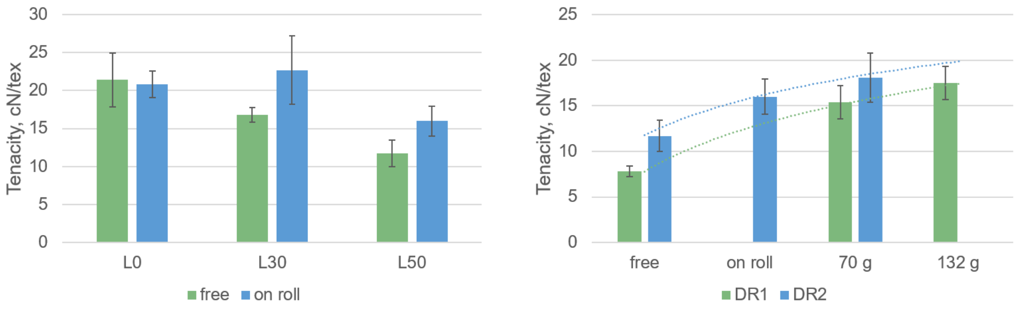


Figure 5.6: Mechanical properties fiber precursors. On the left, variation between different lignin ratios and drying free or on roll. On the right, comparison between DR1 and DR2 for L50 fibers, and different drying conditions.

SEM was used to observe the cross section and surface of the fibers. The cross section was used to examine the shape and diameter of the fiber precursors. Figure 5.7, show the cross section of L0 and L50 precursor fibers dried free. As the image show, L0 fibers have a smaller diameter and also a less cylindrical shape compare to L50 fibers. For L0 fibers there is also a higher amount of double fibers.

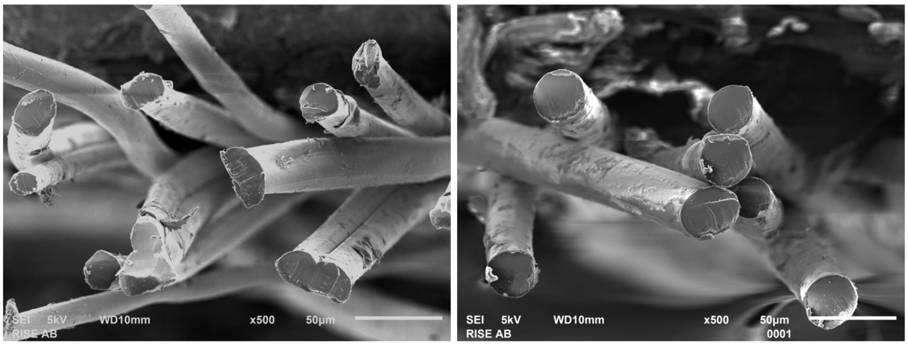


Figure 5.7: Cross section of lignin-cellulose precursor fibers captured with a SEM. On the left, L0 fibers dried free. On the right, L50 fibers dried free.

An average of the diameter of the precursor fibers was obtained from the different methods; using Vibroskop, light microscopy, and SEM. Vibroskop measures the Titer, which is the linear density of the fiber. This can be converted into a diameter by using the density of the fiber. When comparing all diameters, Appendix A, fibers dried free had a higher standard derivation. Fibers that are allowed to dry free shrink in the length direction which causes an enlargement of the diameter. The large standard deviation could be the result of an uneven lengthwise shrinkage

5.3 Carbon fibers

The lignin-cellulose precursor fibers spun in this work have been converted to carbon fibers. The analysed properties are summarized in Figure 5.8. The first impression indicates that fibers containing lignin show improved properties for fibers dried with tension. When taking the standard derivation into account, the result is overlapping. Hence, the results indicate that there is no big difference in the mechanical strength between different drying methods. Additionally, there is neither any large difference in strength dependent on the lignin ratio. The reason cellulose fibers do not follow the same pattern is because L0 free and L0 on roll have been spun with DR2 and DR1, respectively. This affect the orientation within the fiber and hence the properties.

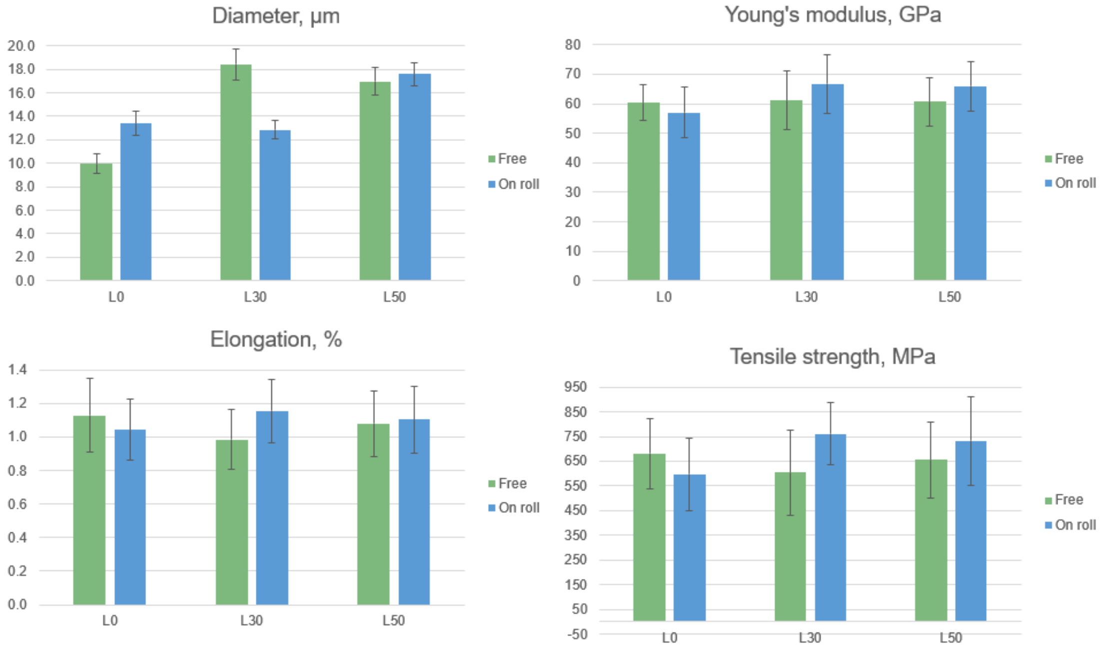


Figure 5.8: Mechanical properties of stabilized and carbonized fiber precursors.

Notable is the high standard derivation, which may correlate with some converted double fibers, mainly L0 fibers, which was detected when analyzing the fibers in light microscopy and SEM. To avoid double fibers, a spin finish can be used, which makes it easier to separate fibers from each other [24]. For measurement of the mechanical properties of the carbon fibers, the diameter of the fiber is measured to calculate the area that is used to define the tensile strength by dividing the applied force by the area. When a double fiber is measured, the diameter becomes doubled, and the area will be fourth times larger than the accrual area of a single fiber, which affect the Young's modulus.

The tensile strength of precursor fibers and carbon fibers can be compared by conversion to SI units (Pa) for fiber precursors. This have been done by conversion of the linear density (titer) to area based on the density of the fibers. The tenacity of L50 fibers dried free and on roll, 12 and 16 cN/tex correspond to a tensile strength of 143 and 195 MPa. The tensile strength for all fibers are shown in Appendix A. When comparing to the tensile strength of converted carbon fibers with tensile strength of 655 and 733 MPa, the conversion make the fiber about three times stronger.

The dried L50 fibers, both dried free and on roll, were converted to carbon fibers in crucibles to determine the gravimetric yield. The results of the total yield are summarized in 5.4. The yield is not normalized to the dry content. When normalizing against the dry content, around 95%, the yield is about 32% for both samples. This is comparable to earlier studies that have a similar yield for fibers with a lignin-cellulose ratio of 50/50 [26]. The theoretical carbon yield for a pure cellulose fibers is around 44%, however, due to depolymerization of macromolecular chains the actual yield is around 10-30% [18].

Table 5.4: Total yield of converted L50 fibers to carbon fibers.

Stage	L50 free	L50 on roll
Initial mass (mg)	123.5	82.0
Mass stabilized fiber (mg)	104.0	70.2
Stabilization yield ($wt\%$)	84.2	85.6
m carbonized fiber (mg)	38.0	24.8
Carbonization yield ($wt\%$)	36.5	35.3
Total yield ($wt\%$)	30.8	30.2

6

Conclusion

This investigation shows that thermoporometry is a useful method for analysis of lignin and cellulose fibers. The combination of using WRV together with thermoporometry gives an additional dimension of the analysis. WRV gives an indication of the entire pore volume of the fiber while thermoporometry gives a measure of the pore size distribution of pores between 2-200 nm. An additional advantage with both the thermoporometry method and WRV is that both never dried and dried fiber can be analysed. This make the method suitable for analyse of drying step. Further, with thermoporometry the pore size distribution can be analysed which is not possible with WRV.

When comparing the result from the WRV and thermoporometry, the difference gives a indication of pores larger than 200 nm. For never dried fibers this difference is larger compared to dried fibers. From this it can be concluded that the larger pores is the ones collapsing or enclosure up on drying.

Mechanical properties of different precursor fibers showed that tension during drying is of high importance. Especially when the fiber contained both lignin and cellulose, a major change in the mechanical properties was obtained. The increase in the mechanical strength was 36% for L50 fibers produced with DR2 dried with tension on roll compared with dried free. Related to no significant difference of porosity seen in the result from the thermoporometry measurements, the increased strength is not related to the porosity. Instead it may be related to a more structured molecular orientation.

Indication of increased mechanical strength for carbon fibers made from precursors dried with tension was also found, but the high standard derivation made it difficult to draw a conclusion of how the tension affect the mechanical properties of carbon fibers. Related literature have shown increased mechanical strength for precursor fibers when increasing the tension during spinning and stabilization.

A optimization between applied tension during spinning, drying and stabilization have to be further investigated to gain better mechanical properties, and the change of replacing today's commercialized carbon fibers.

7

Future work

This work have given lots of new information of how mechanical strength and porosity are affected upon drying. But there are parts that are interesting to look at further. These are stated here below:

- Is is beneficial to use more tension during drying and can it be made in a continuous way and further industrial? Indication of increased mechanical properties have been observed in this thesis, but can more tension be used and how much? And can more tension affect the porosity in the fibers?

- Tension during drying have shown to increase the tenacity and modulus, previous studies have given an indication of increased tenacity and modulus with increased draw ratio. How can these be combined? How much draw ratio could be used to maximise the tension during drying?

- Analyse how the lignin in the fibers affect the absorption of water? Could any other solution be used instead?

- How thick is the NFW layer? Different studies use different thicknesses of NFW and this is because there is no known thickness because of different interaction between the surface and the water because of different properties of the material.

Bibliography

[1] B. A. Newcomb, "Processing, structure, and properties of carbon fibers," *Composites Part A: Applied Science and Manufacturing*, vol. 91, pp. 262–282, 12 2016.

[2] N.-D. Le, M. Trogen, Y. Ma, R. J. Varley, M. Hummel, and N. Byrne, "Understanding the influence of key parameters on the stabilisation of cellulose-lignin composite fibres," *Cellulose*, 2020.

[3] A. Bengtsson, J. Bengtsson, M. Sedin, and E. Sjöholm, "Carbon Fibers from Lignin-Cellulose Precursors: Effect of Stabilization Conditions," *ACS Sustainable Chemistry and Engineering*, vol. 7, pp. 8440–8448, 5 2019.

[4] M. Ek, G. Gellerstedt, and G. Henriksson, *Pulp and Paper Chemistry and Technology - Wood Chemistry and Biotechnology, Volume 1*, vol. Volume 1. Stockholm: De Gruyter, 2009.

[5] A. Bengtsson, J. Bengtsson, C. Olsson, M. Sedin, K. Jedvert, H. Theliander, and E. Sjöholm, "Improved yield of carbon fibres from cellulose and kraft lignin," *Holzforschung*, vol. 72, pp. 1007–1016, 12 2018.

[6] O. Bahl, Z. Shen, J. G. Lavin, and R. A. Ross, "Manufacture of Carbon Fibers," in *Carbon Fibers, Third Edition* (J. Donnet and R. Bansal, eds.), vol. 3, pp. 1–85, New York: Taylor & Francis, 1998.

[7] E. Frank, L. M. Steudle, D. Ingildeev, J. M. Spörl, and M. R. Buchmeiser, "Carbon fibers: Precursor systems, processing, structure, and properties," 5 2014.

[8] C. Olsson and G. Westm, "Direct Dissolution of Cellulose: Background, Means and Applications," in *Cellulose - Fundamental Aspects*, InTech, 8 2013.

[9] M. Ek, G. Gellerstedt, and G. Henriksson, "Pulping chemistry and technology," *Pulping Chemistry and Technology*, pp. 1–471, 12 2009.

[10] S. Chatterjee and T. Saito, "Lignin-Derived Advanced Carbon Materials," 12 2015.

[11] F. Öhman, H. Wallmo, and H. Theliander, "A novel method for washing lignin precipitated from kraft black liquor - Laboratory trials," *Nordic Pulp nad Paper Research Journal*, vol. 22, no. 1, 2007.

[12] M. Hummel, A. Michud, M. Tanttu, S. Asaadi, Y. Ma, L. K. Hauru, A. Parviainen, A. W. King, I. Kilpeläinen, and H. Sixta, "Ionic liquids for the production of man-made cellulosic fibers: Opportunities and challenges," *Advances in Polymer Science*, vol. 271, pp. 133–168, 2015.

[13] C. Olsson, E. Sjöholm, and A. Reimann, "Carbon fibres from precursors produced by dry-jet wet-spinning of kraft lignin blended with kraft pulps," *Holzforschung*, vol. 71, pp. 275–283, 4 2017.

[14] F. Liu, H. Wang, L. Xue, L. Fan, and Z. Zhu, “Effect of microstructure on the mechanical properties of PAN-based carbon fibers during high-temperature graphitization,” *Journal of Materials Science*, vol. 43, pp. 4316–4322, 6 2008.

[15] A. Sharma, D. Sen, S. Thakre, and G. Kumaraswamy, “Characterizing Microvoids in Regenerated Cellulose Fibers Obtained from Viscose and Lyocell Processes,” *Macromolecules*, vol. 52, pp. 3987–3994, 6 2019.

[16] S. Park, R. A. Venditti, H. Jameel, and J. J. Pawlak, “Changes in pore size distribution during the drying of cellulose fibers as measured by differential scanning calorimetry,” *Carbohydrate Polymers*, vol. 66, pp. 97–103, 10 2006.

[17] J. M. B. Fernandes Diniz, M. H. Gil, and J. A. A. M. Castro, “Hornification-its origin and interpretation in wood pulps,” *Wood Sci Technol*, 2004.

[18] A. Gü Mrah Dumanlı and A. H. Windle, “Carbon fibres from cellulosic precursors: a review,” *Journal of Materials Science*, 2012.

[19] F. Gu, W. Wang, Z. Cai, F. Xue, Y. Jin, and J. Y. Zhu, “Water retention value for characterizing fibrillation degree of cellulosic fibers at micro and nanometer scales,” *Cellulose*, vol. 25, pp. 2861–2871, 5 2018.

[20] H. Zhang, Z. Li, S. Yang, W. Zhang, Y. Sun, S. Chen, and C. Luo, “Comparison of Some Key Parameters Contributing to Lignocellulosic Fiber Deformation Behavior by a Mathematical Model,” *BioResources*, 2019.

[21] T. C. Maloney, “Thermoporosimetry of hard (silica) and soft (cellulosic) materials by isothermal step melting,” *Journal of Thermal Analysis and Calorimetry*, vol. 121, pp. 7–17, 7 2015.

[22] L. Salmén and J. S. Stevanic, “Effect of drying conditions on cellulose microfibril aggregation and “hornification”,” *Cellulose*, vol. 25, pp. 6333–6344, 11 2018.

[23] S. Park, R. A. Venditti, J. J. Pawlak, and H. Jameel, “High Resolution Thermogravimetric Analysis of Pulp Drying,” *Trans. of the XIIIth Fund. Res. Symp. Cambridge*, pp. 161–186, 2005.

[24] J. Bengtsson, *Air gap spinning of lignin cellulose fibres.* PhD thesis, Chalmers University of Technology, Gothenburg, 2021.

[25] N. Garoff, R. Protz, J. Erdmann, J. Dr. Ganster, and A. Dr. Lehmann, “patent,” 2016.

[26] A. Bengtsson, J. Bengtsson, K. Jedvert, M. Kakkonen, O. Tanhuanpää, E. Brännvall, and M. Sedin, “Continuous Stabilization and Carbonization of a Lignin-Cellulose Precursor to Carbon Fiber,” *ACS Omega*, 2022.

A

Appendix 1

Table A.1: Conversion to SI units from tensile strength of fiber precursors.

	Titer, dtex	Dencity (g/cm^3)	Diameter, um	Area, m^2	MPa
L0 free	4.6	1.2992	21.3	3.55E-10	268
L0 on roll	8.4	1.3621	28.1	6.18E-10	281
L30 free	13.9	1.2517	37.7	1.11E-09	210
L30 on roll	5.9	1.2648	24.4	4.68E-10	276
L50 free	13.2	1.2489	36.7	1.06E-09	143
L50 on roll	10.7	1.2407	33.2	8.65E-10	195

Table A.2: Diameter of fiber precursors measured by Vibroskop, light microscope and SEM. Including standard derivation of the measured diameters.

	Titer	Light microscopy	SEM	STD
L0 free	21.3	19.8	20.2	0.61
L0 on roll	28.1	27.6	24.9	1.39
L30 free	37.7	32.5	30.7	2.94
L30 on roll	24.4	24.9	24.4	0.25
L50 free	36.7	31.7	27.7	3.69
L50 on roll	33.2	29.5	33.7	1.87

Table A.3: Measured diameter of L50 fibers, never dried, dried and re-wet using light microscopy. Diameter measured in µm and converted into a volume assuming cylindrical shape and a length of 1. Using volume to prove the impact of an increase in diameter. The unit of volume is μm^3

	Drying	Diameter	+/-	Volume
L50 ND		58	5.1	2626
L50 free	dry	32	2.1	788
	re-wet	40	2.3	1281
L50 on roll	dry	29	2.0	683
	re-wet	40	1.5	1272

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden
www.chalmers.se

CHALMERS
UNIVERSITY OF TECHNOLOGY